Hydrocarbons from Carbide (A) V. Non-catalytic Polymerization under Elevated Pressures[1]. Comparison between Ordinary and Elevated Pressure Reactions.

By Ryoji NEGISHI and Osamu KAMIIKE.

(Received April 6, 1942.)

In Papers (A) II to IV[2], inclusively, we have given rather in detail the results of non-catalytic direct synthesis of hydrocarbon liquids from calcium carbide under ordinary pressure, and with the valuable informations gained therefrom, we have now attempted the same synthesis but under elevated pressures. The experimental results and discussions have been already given in Japanese[1], and in this paper we shall summarize only the main features of the three original papers, including also the additional discussions which are not found in the above papers[1]. The treatment of the general subject, the synthesis of hydrocarbon liquid products directly from calcium carbide, will be made as complete as possible, however, always in harmony with the reliability and completeness of our experimental results which, we must admit, are not quite satisfactory at places.

Under elevated pressures we have limited our investigations to hydrogen-carbide, carbon monoxide-carbide, and a few preliminary runs with carbon dioxide-carbide systems. What prompted us to study these systems were the following questions: (1) Would the products from the carbide contain more hydrogen when they are prepared in excess of it? (2) What would be the behaviour of nascent acetylene towards hydrogen? (3) What are the effects of carbon monoxide (and water gas) particularly on the total liquid yield? (4) What differences exist between the runs under low and elevated pressures?

Before answering these questions, it would be of advantage to touch on some of the experimental details which are necessary for understanding and appreciating the difficulty involved and for estimating the reliability to be expected of the results.

For these high pressure experiments, three one liter autoclaves, which could be only used for static experiments, had been used. As a practical means of furnishing the necessary water for the carbide reactions, aluminum hydroxide, which gave up most of its water in the temperature range, 200 to 300°C, was used. Because of these limitations, the results obtained were limited both in scope and significance.

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(1) This subject will be presented by the authors and M. Nibayashi in detail in Japanese in a series of Papers I to III, which will appear in *J. Soc. Chem. Ind., Japan*, **45**(1942). In the present paper most of the experimental details and tables will be omitted and only the high-lights of the three papers, which will henceforth be referred to as Papers I, II, and III, will be summarized.

(2) R. Negishi and O. Kamiike, this Bulletin, **17**(1942), 118; *ibid.*, **17**(1942), 44; *ibid.*, **17**(1942) to be published.

Some of the difficulties and uncertainties involved in these experiments will be mentioned briefly. First of all, heating of the autoclave had to be very carefully controlled to maintain the temperature in the range where aluminum hydroxide gave up most of its water. Since the reactions between calcium carbide and water are rapid and highly exothermic, if the release of the water is too rapid, there are apt to occur sudden "jumps" both in temperature and pressure. One example given below illustrates the "jumps" effectively. Initially, carbide grains of 2–3 mm. diameter and 100 kg/cm^2. of hydrogen were employed.

Exp. No.	Just before Jump		Just after Jump		C/H in Residue	Vol. % of $CH_4+C_2H_6$
	Temp. (°C.)	Press. (kg./cm^2.)	Temp. (°C.)	Press. (kg /cm^2.)		
I_A-7	260	163	433	279	19	57.6

If powdered carbide is used, the jumps are more pronounced. They take place in less than one minute. When they occur, no liquid products, but saturated gases mostly of low molecular weight, and a large amount of free carbon in the residue are formed. Jumps were prevented to a large extent by using grains and by separating the hydroxide catalyst from the carbide by charging the former in a cylinder supported at the center of the autoclave. The hydroxide catalyst thus charged will be referred to as "in cylinder".

The second difficulty encountered was in obtaining satisfactory weight and carbon balances. Needless to say, our runs under elevated pressures were less refined than those under ordinary pressure, but besides this difference in the experimental refinement, there were at least two outstanding sources of difficulty. One of them was associated with the fact that the autoclaves had to be opened and closed after each run, and small leakage was often undetected. This probably accounted for the chief uncertainty in the weight balance. Uncertainty in the residue analysis was presumably the largest factor which gave unsatisfactory results in the carbon balance.

The residue consisted of free carbon, very high polymers, unreacted carbide, carbonate, calcium oxide, and small quantities of sulfur and other compounds. We found no satisfactory method of analysis. Our method was to extract the residue with chloroform and then to react it with water to determine the unreacted carbide; then with either dilute HCl or acetic acid to determine the carbonate content. The acetate or the chloride formed was dissolved with excess of water, and after drying, the residue was subjected to elementary analysis. It was quite difficult to oxidize the residue completely, and often very severe conditions, which were not without harm to the reagents in the combustion tube, had to be employed. Evidence of incomplete combustion of the sample was often noticeable.

While our blank runs indicated that below 400°C autoclaves II and III, which were used in most of the runs of our series, were practically

without any catalytic effect* for carbon monoxide and hydrogen mixtures, autoclave I was appreciably catalytic already at lower temperatures for the reduction of CO into methane and H_2O. Above 400°C the catalytic effect of each autoclave was more apparent, but the character of the reactions remained the same. When CO and H_2 were mixed with carbide alone, some hydrocarbon liquid products were obtained, but this was accounted for by the reactions:

$$CO + H_2 \rightarrow \text{methane and ethane} + H_2O$$

$$H_2O + CaC_2 \rightarrow CaO + C_2H_2 \text{ Polymerize into liquid products.}$$
(and Carbonate)

Under similar conditions similar results were obtained, and the less the catalytic effect, the more reproducible were the results. These facts indicated that most of our runs were sufficiently reliable, and most of the differences in the carbon and weight balances were due to the factors considered above. It may be inferred, therefore, that when the total weight balance does not deviate a great deal from 100%, the results are, except for the residue analysis, nearly correct, regardless of what the corresponding total carbon balance may indicate. For the comparison of the gaseous and liquid products, therefore, it is the total weight balance, and not necessarily the carbon balance, that serves as a guide as to the reliability of the data. Our temperature readings are probably good to about ±5°C and the pressure within ±5 kg/cm². In our present investigations, accuracy of 5% would be as satisfactory as might be hoped for, and even an order of 10% must be considered rather satisfactory.

Discussion. The results of blank runs on the catalytic effects of the autoclaves have been reported in Paper I, and those of the systems, hydrogen-carbide and carbon oxides-carbide, have been given in Paper II. We shall not retabulate the results here, but immediately avail ourselves of answering the questions raised at the beginning of this paper. The answers will not be given in the order of the questions.

(A) Effects of Pressure and Temperature. (1) *On the Yield of Products.* Results under various total initial pressures of the runs made with hydrogen, carbon monoxide (or water gas), and carbon dioxide are given in Table 20. Most of our runs were made in the neighborhood of 100 atmospheres, since it was evident from the hydrogen system that at about this pressure, a maximum in the total liquid products (free of gases condensed and dissolved in the trap and extractable products from the solid residue) was found. The existence of this maximum may have some connection with the concentration of the acetylene available. Although the total liquid products seem to be a direct function of the total pressure, the yields of saturated gases** are rather a function of the partial pressure of hydrogen. This is to be expected. The percentage yield of liquid products based on the

* For a more detailed description of the effect, see Ref. 1, particularly Paper I.

** Those of olefins and acetylene are small and the results are less definite.

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Table 20. Effect of Pressure and Temperature on Products.

(Max. Reaction Temp. ≃ 450°C.)

Exp. No.	Total Initial Press. kg./cm². at Room Temp.	Partial H_2 Press.	% Calculated on Reacted CaC_2 Carbon			Wt. (g.) Carbonate Carbon in Residue*	Note	Gas
			Methane+ Ethane Carbon	Residue Carbon	Liquid Carbon			
I_A 14	25	25	16.9	55**	23.6	< 3.8Ω		H_2
I_A Ser. 26	50	50	29.3	27.6**	26.6	<17Ω		
I_A Ser. 37	50	50	19.7	25.6**	28.4	<15Ω	"in cylinder"	
I_A Ser. 16	100	100	42.0	5.8	32.8	2		
II_A Ser. 38	100	100	32.6	4.4	33.3	1.3		
I_A 1	200	200	49.5	7.3**	24.9	< 4Ω	Calcd. on 200 grs.	
II_A 15	70	53	27.6	6.7	22.1	4.3		$CO+H_2$
II_A 11	70	50	25.2	13.8	22.2	9.3		
II_A Ser. 21	100	56	22.7	10.6	23.1	23.1		
I_A Ser. 51	100	∞80	23.2	21.4	36.8	25.8		$CO+H_2$
II_A Ser 18	70	∞55	10.1	17.2	12.6	14.4	405°C.	$CO+H_2$
III_A Ser. 57	180-150***	∞50	24.4	12.7	25.0	26.7	370°C.	

* Calculated on 60 grams of reacted carbide carbon.
** Contains carbonate carbon.
Ω Contains residue carbon.
*** At 370°C.

reacted carbide carbon of the elevated pressure runs are appreciably higher than the corresponding ones of ordinary pressure. We believe that this apparent increase in the yield is due to temperature effects than to any change in the reaction mechanism. In the autoclave runs any solid products, such as the yellow powder formed at lower temperatures and heavy liquid products adsorbed on the solid, are either decomposed into liquid or distilled out at higher temperatures, e.g., 450°C. On the other hand, in the runs under ordinary pressure, any such products will remain in the residue. Support for this argument is found in the relatively small amounts of carbon in the solid residues of the runs of high as compared with those of the low pressure, as shown in Table 15 (Paper (A) IV) and Table 20. Another evidence of this can be got from the results of II_A–Ser. 18 in which the highest temperature is 405°C. There, the percentage of liquid products is very much smaller, but the residue contains about 15 g. of extractable liquid as compared with a few grams from the others at 450°C. The results of III_A–Ser. 57, which will be discussed further in detail later, illustrate the same point.

(2) *On Hydrogenation.* In Table 21 the ratios of H/C, corrected and not corrected for methanol oxygen (Paper (A) III), of the condenser condensates of the runs under low and high pressures are given. In the last row of the table, percentages of hydrogenation based on the H/C ratio of acetylene for the different gases used are shown. It is evident

Table 21. Degree of Hydrogenation of Condenser Condensates.

System	Low Pressure			Elevated Pressure		
Gas	H_2	$CO+H_2$	CO_2+H_2	H_2	$CO+H_2$	CO_2+H_2**
H/C×10 Found	1.101	1.026	1.018	1.173	1.276	1.122
H/C×10 Corrected* ..	0.905	0.890	0.858	0.973	1.091	0.833
% Hydrogenated based on H/C of Acetylene.	8.7	6.8	3	17.5	31.0	0

* Corrected for methanol oxygen.
** Result of one run.

that under elevated pressures, the percentages are higher. It is very much higher for $CO+H_2$ system while it is, within our experimental accuracy, about the same for CO_2+H_2 system. Furthermore, it seems that in the latter system the pressure has practically no effect. The fact that among the runs under high pressure, the degree of hydrogenation is almost independent of the pressure, within the range investigated, seems to strengthen our belief that the mechanism of the nascent acetylene polymerization is highly specific and but slightly—if at all—affected by pressure. The apparent increase in the percentages must be due to an increase in the time of contact. While in the runs under ordinary pressure it is about 20 sec, in the autoclave runs the substances remain in contact with hydrogen over 100 minutes. A particular increase in the H/C ratio for $CO+H_2$ system may be due to a slight formation of liquid product from water gas under elevated pressures. This statement appears paradoxical to what we have mentioned in Paper I that the gas itself does not form any liquid products. Since the conditions involved in the blank and present runs are quite different in such factors as the time of contact, the reaction products, it may be quite possible that a negligible amount in the blank runs could have become a bit more appreciable in the present runs, where especially any catalytic tendency will be greatly enhanced by the presence of the carbide[3]. Or it may be in some way connected with the presence of the reactive hydrogen* produced by some such reaction[4] as

$$CaO + H_2O + CO = CaCO_3 + H_2, \quad (A)$$

which is a combination of

$$H_2O + CO = CO_2 + H_2 \quad \text{and}$$

$$CaO + CO_2 = CaCO_3.$$

We have seen that both of these reactions take place readily in our systems. According to Ellis[4], the first reaction, (A), so-called "lime process", takes place most readily under elevated pressures and at about

(3) R. Negishi, O. Kimura, and O. Kamiike, *Rev. Phys. Chem., Japan*, 15(1941), 31.

(4) C. Ellis, "Hydrogenation of Organic Substances," 3rd Ed., 738, D. Van Nostrand Co., N. Y., (1930).

* We have seen the same sort of evidence in the runs under low pressure (2).

450–600°C. The fact that $CO+H_2$ may have reacted under elevated pressures to produce some liquid products becomes more probable, though not necessarily more conclusive, in the light of the results of III_A Ser. 57. In this run the reaction temperature was constant at 370°C, and water gas was charged 5 times at the reaction temperature to maintain the total pressure to 160–180 kg/cm². The time of reaction was 1600 minutes. A liquid product condensed at 370°C was over 9 g. and 25% of the total reacted carbon, assuming that all the carbon had come from the carbide.* These values represent in percent and in the absolute amount a maximum at such a low temperature. A word should be added that in this run a catalyst, which was, however, found quite inactive,** had been used, and this fact cannot be entirely over-looked in the above discussion.

(B) **Products.** (1) *Liquid.* The combined liquid products from the runs under high pressure were separated into three groups: those obtained when aluminum hydroxide was in contact with the carbide, the hydroxide "in cylinder", and those obtained with water gas mixtures. Their distillation curves and a similar one for the runs under low pressure are shown in Fig. 3. It is interesting that the curves for the runs under low pressure and the hydroxide 'in cylinder" are alike in many respects. This is probably due to the temperature effect. This is in accord with thermodynamic considerations[3]. When the hydroxide and the carbide are separated, i.e., the hydroxide is "in cylinder", the water vapor released must diffuse through the atmosphere of the gas and the concentration of the water molecules must be uniformly distributed throughout by the time they react with the carbide. If, however, the hydroxide is in intimate contact with the carbide, the concentration of the water molecules may not be uniform, but may be larger at places, and there the temperature may be higher than the average of the system. This explanation seems

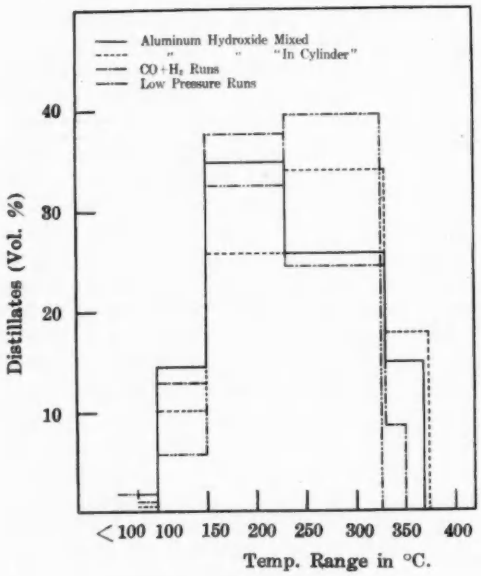

Fig. 3. Distillation Curves.

* This assumption seems reasonable (Papers (A) III and II).

** As will be explained in one of the subsequent papers to be published elsewhere that even a slightly active catalyst may become rather active in the presence of the carbide.

to suffice for the shape of the curve for the liquid obtained when the hydroxide is in mixture with the carbide. The fact that its curve is similar to that of the water gas system may be accidental. As has been mentioned in a preceding section, CO and H_2 may have formed some liquid products which boil at lower temperatures. III_A Ser. 57 is a good example.

No detailed chemical analysis of the products has been made, but from some of the physical constants determined, they are chiefly aromatic and condensed in nature, as in the case of the runs under low pressure. From what has been said above, it seems quite probable that the main reaction of the nascent acetylene molecules under elevated pressures (under our present limited conditions) is the same as that under ordinary pressure runs, and the minor differences are ascribable to temperature and side effects, such as the formation of liquid products from the carrier gas itself, independently of the main reaction. The elementary analyses of the products are given in Tables 5, 7, and 9 in Paper II.

So far in these papers, we have reported only those runs made with aluminum hydroxide, but we have made some with zinc hydroxide as well. The results of the latter will be now given briefly. The yield of liquid products was about as satisfactory, and the products appeared more stable than those with aluminum hydroxide; their colour* did not change on standing, even over a year, and they appeared to be more hydrogenated. It seemed that zinc hydroxide had some catalytic effects[5].

(2) *Gas.* The results of gas analysis of the runs are given in Tables 2, 3, 6, 9 and also in Paper II. It may be of some interest to mention that in some of the runs, especially when the total pressure of the system is low, the gaseous products** (at room temperature) found in the trap may be as high as 1/4 of the total original condensates (gaseous products condensed in trap and liquid products), as in runs II_A–13, II_A–11, and I_A Ser. 23; about 1/5 for I_A Ser. 37***. The analyses of the gases found in the trap are given in the same tables. It may be of some interest to note that their compositions are chiefly propane, butane, and olefines.

(3) *Residue.* The carbon content of the residue was small in every case when hydrogen was used and was also rather small for the other systems when that due to the carbonate carbon was taken account of. It is significant that the carbonate carbon contents are small in the hydrogen system, larger in the carbon monoxide (or water gas) system, and

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* Amber, reddish, clear, and less dark than with aluminum hydroxide.

(5) A. J. Lozovoi, *Gen. Chem.* (USSR) **1**(1931), 717. He had found that zinc oxide showed some catalytic effect in the polymerization of ordinary acetylene molecules, and it produced a liquid product at 370°C while aluminum oxide was much less catalytic and it did not reduce the ordinary temperature (500–600°C) of liquid formation.

** Condensed and dissolved in the trap cooled with alcohol-solid carbon dioxide.

*** Conditions of Runs.

Run	Gas	Total Press. kg./cm². (Room Temp.)
II_A 13	CO and H_2	37
II_A 11	,,	70
I_A Ser. 23	H_2	25
I_A Ser. 37	H_2	50

its value is, indeed, about the same as that of the carbon dioxide system when the time of contact is sufficiently long. As has been said before, the yield of liquid products increases at the expense of the carbon content in the residue. This is evident in Table 20.

(C) **Limitations of the Results.** As has already been mentioned in Paper I, the results obtained here are limited both in scope and significance because of the limitations imposed on the experimental conditions. Since aluminum hydroxide gives up most of its water at 200 to 300°C, the main reaction of the water vapor and the carbide is the formation of yellow powder[6], or a cuprene-like substance, the formation of which is influenced only slightly by the variation in the gases employed. Above 300°C the apparent formation of the liquid products is due to a sort of distillation effect which is again only a little affected by the species of the gases. On account of these factors, it is but natural that the differences owing to pressure, temperature, and species of gases are not as clearly marked as they would be if a proper choice in the apparatus has been made. Since we now possess an autoclave in which the water vapors can be made to react with the carbide under any desired temperature and pressure, we are certain that more significant results are possible.

The carbide reactions are characterized by a large evolution of the heat of reaction, and this heat must be taken away rapidly and effectively in order to obtain a maximum benefit from the use of carbide. Problems concerning the utilization of the heat of reaction will be the subject of a subsequent paper.

(D) **Couclusion.** The use of nascent acetylene to bring about more effective polymerization, and the use of the carbide as a means of promoting and accelerating many organic syntheses which otherwise would be thermodynamically improbable are new problems that have not been heretofore investigated at all, or but slightly.

Therefore, in this series of investigations it has been the intention of the authors to study these problems rather broadly, but still sufficiently in detail to obtain data which are of fundamental interest and to see further what practical possibilities are open to them.

The polymerization of nascent acetylene has been made under ordinary pressure in dynamic system and under elevated pressure in static system. The data obtained are somewhat fragmentary because of the explorative nature of the investigation, of the extensiveness of the field to be covered, and finally of the limitation imposed on the experimental conditions; but they are, nevertheless, sufficient to draw some general conclusions.

First of all, it is safe to conclude that the efficacy of the polymerization into liquid products of nascent acetylene is higher than that, even in the presence of an active catalyst, of the ordinary actylene—a manifestation of very high reactivity of nascent acetylene. For this reaction, the apparatus necessary is quite simple, and the need of a catalyst is dis-

(6) R. Negishi, M. Nibayashi, S. Kataoka, and O. Kamiike, *J. Soc. Chem. Ind., Japan*, **45**(1942), in print.

pensed with. However, the reaction has certain limitations. The final products are almost exclusively aromatic or condensed, as shown by their high densities and boiling points, and they are too diversified to be easily separated into individual components. The course of its polymerization cannot be controlled but with difficulty because of the extreme reactivity and specificity of the reactions of nascent acetylene. It seems to the authors that the production of the paraffin series, as the main products directly from calcium carbide, is not likely unless a catalyst of high selectivity is found. The heat of reaction involving the carbide is enormous, and this factor must be well considered; otherwise, harmful rather than favorable effects of the carbide will take place.

The specificity of nascent acetylene polymerization seems uninfluenced by the presence of foreign substances, and this fact makes possible the use of carbide as a means of clarifying the mechanism of a reaction in which even a catalyst may be present, without the fear of introducing undesirable side reactions involving acetylene and the reactants of the desired reaction. However, the fact that the commercial carbide almost invariably contain sulphur and phosphorus compounds as impurities must not be overlooked when a catalyst is used.

Because of the fact that calcium carbide is a powerful deoxygenating agent by virtue of its strong affinities for water and carbon dioxide molecules, it may be used with advantage in the preparation of deoxygenated products. As an example, it can take off the oxygen from alcohols readily. Butyl alcohols may be prepared from either methanol or ethanol, or both[7], and completely deoxygenated compounds can also be formed from them. Thermodynamically, it is possible to deoxygenate practically all organic compounds, and this should be of great interest as a means of preparing such materials as olefines, unsaturated compounds, ethers, and other useful for organic syntheses.

The introduction of calcium carbide opens up the possibilities of organic syntheses enormously by virtue of its large increase in the free energy of reaction and the shift in the equilibrium owing to its great affinities for water and carbon dioxide molecules, which are not infrequently the by-products of organic reactions. By a proper choice of catalyst and experimental conditions, unlimited number of desirable substances may be synthesized.

Finally, this will conclude a series of investigations on the direct synthesis of hydrocarbons from calcium carbide. Due to circumstance, we are unable to pursue further this investigation and, with regret, we must leave many of the unsolved problems as they are. It is hoped that we shall be able to take up again this investigation from where we must leave off now.

What have been reported by us in a number of papers[1][2] are the results of the culminating efforts of the following members, Messrs. Araki, Hayashi, Inaba, Kano, Kodama, Masunaga, Nagayoshi, Nakano, Sakon, Shimamura, and Shimono. To them our thanks are due. We are grateful to Dr. S. Hamai, Messrs. Nibayashi, Isobe, and Kataoka for their hearty co-operation.

(7) R. Negishi, *Rev. Phys. Chem., Japan*, **15**(1941), 127; *ibid.*, **15**(1941), 171.

The authors acknowledge with pleasure their indebtedness to Prof. T. Marusawa and to Dr. F. Hansgirg for their constant interest throughout this work; to Dr. M. Sato, the director of the institute, for his encouragement and permission for the publication.

Summary.

The effects on the character and yield of liquid products synthesized directly from calcium carbide under elevated pressures, of the species of gases, pressure, and temperature have been summarized. It has been found that the yield of liquid products increases with increasing total pressure of the system up to about 100 atmospheres and then decreases with further increase in the pressure.

The apparent characteristics of the products in carbon monoxide (or water gas) system seem different from the others, and an explanation for this has been given. As in the low pressure runs, carbon monoxide has rather harmful effects while, on the other hand, carbon dioxide has beneficial effects on the yield of liquid products.

There have been found slight differences in the yields and the properties of the products under elevated and ordinary pressures, and these differences have been explained as due rather to the effects of the time of contact and temperature than to any change in the mechanism of the polymerization reaction.

The limitations and the significance of the synthesis of hydrocarbon liquids directly from calcium carbide and several unique properties of the carbide which may be useful in organic syntheses have been pointed out and discussed.

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The Synthesis of Iso- and Normal Butyl Alcohols in the Presence of Calcium Carbide (B) IV*. Synthesis in Liquid Paraffin. Static System.

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(Received May 12, 1942.)

It has been shown in one of my papers that a large amount of heat is evolved when calcium carbide reacts(1). In dry system the localization and accumulation of heat result, augmenting unfavourable side reactions.

* This paper will appear in Japanese in *Rev. Phys. Chem. Japan*, **16**(1942).

(1) Under certain tolerable assumptions, the heat of reaction evolved at 310°C for autoclave run III_A Ser. 113 has been calculated to be about 114 kcal./mole of 70% carbide reacted.

In order to mitigate these effects, I have attempted to carry out the synthesis of butanols in the presence of calcium carbide in a liquid medium, and the results obtained are presented here. A comparison of these results and those of the dry systems[2] will be given in my next paper, and here, I shall be concerned more with the gaseous products.

Experimental Details[3]. (1) *Method.* The same one-liter revolving autoclave used in the dry systems was again employed. A mixture of carbide and catalyst, both of 60 mesh powders, was charged; liquid paraffin was then added, and the components were mixed. The air in the autoclave was flushed out several times with the reaction gas (or hydrogen), and the temperature was raised to a desired point. The reaction gas was then charged and recharged as often as necessary to maintain the pressure range within the proper limits. Usually, two or three chargings, at or at slightly lower than the reaction temperature, were made for each discharge. Except for the final discharge of the final run of a series, the products were discharged to two or three atmospheres in order to prevent, to a maximum degree, a loss of the medium. The products were condensed as before[2].

(2) **Materials.** (a) *Carbide.* Its final acetylene content, under the standard conditions, was from 70 to 75%. A typical analysis showed:

Subst.	CaC_2	CaO	SiO_2	Al_2O_3	Fe_2O_3	Others*
Weight (%)	72	14.5	3.5	2.4	0.6	7.1

* They contained $CaCO_3$ and some sulphur and phosphorus compounds.

(b) *Liquid Paraffin.* A commercial product was distilled under 5 mm Hg pressure in CO_2 atmosphere[1], and all the light boiling substances, which distilled out when the liquid temperature in the flask was maintained constant at 250°C, were eliminated. Under the standard conditions, the temperature of the liquid corresponded to 430°C, and the maximum vapour temperature attained was 410°C. The whole apparatus was of Terex glass. The elementary analysis of the liquid, designated as Paraffin Oil III, showed:

C=85.55, H=14.08, O=0.37 (by difference).

(c) *Gases.* Water gas was prepared by a technical method. It was used without purification. Hydrogen was a commercial product of about 98% purity. No purification was effected.

(d) *Catalysts.* The catalyst used are given in Table 1. Their preparations were the same as those given in Paper (B) III[2].

Some effects on the catalytic activity of thorium will be mentioned briefly. As Fig. 1 indicates, a small concentration of thorium increases the total yield, and there is an optimum content which lies in the range,

(2) R. Negishi, Paper (B) III, this Bulletin, **17**(1942), 179.

(3) The writer is grateful to Messrs. Sakon, Araki, Simono, and Kano for their experimental assistance.

Table 1.

Methanol Catalysts, their Composition.

(Reduced with H_2 at 400°C. for 4 hours.)

Catalyst No.	Composition in Mole Ratio	Precipitating Agent	Activity*
18ab	Zn : Cr : Th 1 : 1 : 0.05	6 molal K_2CO_3	Good
21	Zn : Cr 39 : 61	25% NH_3	Fair
36a	Zn : Cr : Th 1 : 1 : 0.2	40% K_2CO_3	Good
25	Zn : Cr 39 : 61	28% NH_3	Fair

* Relative, based on the total liquid products, including water, and higher boiling substances.

0.05 to 0.20 moles[4]. The effect on the character of the products of thorium seems but slight, as may be seen from the results given in Table 2.

Autoclave runs $VIII_A$ Ser. 6 and $VIII_A$ Ser. 11 were made, respectively, in the closed autoclaves II and III and both runs extended over 40 hours in 15 days. II_{CA} Ser. 68 was made with a catalyst in pellets (50 g. of which occupied about 40 c.c.), packed in a reaction tube of 2.5 cm. diameter and with space velocities varying rom 3000 to 13500; the reaction period was 95 hours, extending over 12 days.

We shall continue to investigate the effect of thorium and soon we may be able to state with more assurance the real effect of it. At this stage of progress, however, we can merely say that a small amount of thorium seems beneficial, as far as the total yield[5], but not necessarily methanol, is concerned.

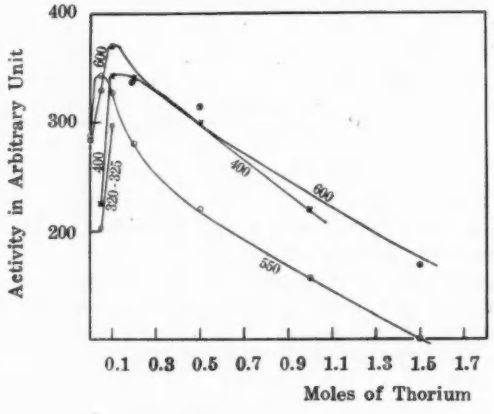

Fig. 1. Activity vs. Thorium Content (Temp. °C. of Reduction Indicated in Fig.)

(3) *Analysis*[6]. Gaseous, liquid, and solid products were analysed as before[7][8]. The solid residue was separated from the medium by washing with ether and filtering under vacuum. The amount of the medium was then determined by evaporating off the ether under reduced pressure. The acetylene and carbo-

(4) No effect of the temperature of reduction has been taken into account, but it is evident in the Fig.

(5) This is important, since in our case, not only the formation of the butanols but also that of hydrocarbons, as by-products, is not undesirable.

(6) The writer's thanks are due to Mr. O. Kamiike and to his assistants.

(7) O. Kamiike, S. Kataoka, M. Nibayashi, and R. Negishi, *J. Soc. Chem. Ind., Japan*, **44**(1941), 1030.

(8) R. Negishi, M. Nibayashi, K. Sakon, and O. Kamiike, *ibid.*, (1942), 366.

Table 2. Methanol from Various Catalysts.

(Water gas used without purification; $CO:H_2$ about 1:1.25)

Exp. No.	Catalyst No. and Composition*	Vol. Methanol*** (%)	Vol. Other Prods.** (%)	Reaction Conds. Temp. (°C.)	Reaction Conds. Press. Kg./cm².
Auto. $VIII_A$ Ser. 6	66, Cr:Zn 1:1	88.5	2.7	320	200–170
Auto. $VIII_A$ Ser. 11	67, Cr:Zn:Th 1:1:0.1	86	3.5	320	200–170
II_{CA} Ser. 68 (t8–86)****	II_{CA} Cr:Zn:Th 0.4:0.6:0.05	85–88	10	330	200

* Mole ratio.

** Consist mostly of water and hydrocarbons; distillation losses not included.

*** Based on total liquid products.

**** Runs 68 and 69 not included. These runs were made at space velocities of 1000 and 2000, respectively. Their methanol vol. % was about 81, much less than the others made at higher space velocities (3000–13500).

nate contents of the residue were determined by taking average results of a large number of samples of the residue mixture, as discharged (including the medium), which were treated with warm water alone and with phosphoric acid, respectively. Blank tests have shown that this method is not reliable more than to 5% which is, however, sufficient for our present purpose. Lack of accuracy is partially compensated by the simplicity of the method.

Results and Discussion. The experimental conditions and some of the results obtained in the liquid system are shown in Tables 3, 4, 5, and 6. In agreement with what has been found[1] at 330°C but a slight amount of the medium is cracked, as shown in Table 3. It is rather startling that so much condensates have been obtained in the condenser, even at 300°C, in the presence of the carbide. A plausible explanation of this seems that a part of the medium has been forced out rather than cracked and distilled out. This has been definitely the case with runs 82 and 98. There is a trend in the amounts of condenser condensates with the reaction temperatures, but there may be no real significance in this parallelism. However, there is no reason to doubt that the presence of the carbide increases cracking of the medium[1], as seen from the results of IV_A Ser. 139 and IV_A Ser. 124[9]. In the latter run there is 41.7 c.c. of the fractions boiling lower than the original, as compared with only 6.7 c.c. in the former in which no carbide is present.

The results of Table 4 indicate that the lower the reaction temperature, the larger is the amount of the fraction boiling below 230°C. The same sort of relationship exists between the yield of iso-butyl alcohol and the temperature, as seen from Table 5. With decreasing temperature, however, the rate of reaction becomes quite slow.

(9) The results of this series are sufficiently reliable, and their quantitative discussion will be reserved for the next paper to be published in this Bulletin.

Table 6 gives the summarized results of gas analysis. There is no trend in the formations of the gases, except for methane, with temperature. It is of some interest to note that, as in all our carbide reactions, large amounts of ethylene, propane, and butane are present in the condensable gases (the gases condensed and dissolved in a trap cooled with

Table 3. Experimental Conditions.

Exp. No.*			Ser. 178	Ser. 139	Ser. 124	Ser. 58	Ser. 82	Ser. 98
Autoclave Used			II	II	II	III	III	II
$CO:H_2$			1:1.23	1:1.35	1:1.3	1:2	1:1.75	1:1.7
Catalyst No. and Wt (g.)			36a, 45	None	18ab, 45	21, 22	21, 30	25, 30
Carbide (g.)			300	None	300	220	300	301
Paraffin (g.)			300	303	300	220	301	300
Temp. (°C.)			300	330***	330	350	360	340-365
Press. Range Kg./cm^2.			200-150	200	200-160	198-130	200-120	200-120
Time (Min.)			1870	1995	2220	1840	1840	2145
Condensates	Cond.	c.c.	26	2.6	52.2	94.4‡	253.2‡	258.6‡
		g.	—	2.1	40.4	73.6	205.9	208.7
	Trap.	c.c.	21.1	0	35.4	37.4	31.4	19.0
		g.	17.7	0	24	25 5	19.5	12.8
Paraffin in the Residue (g.)			—	292	288	160	102	85
Liquid boiling below Original (c.c.)			—	6.7	41.7	6.7	—	—
Condensed and Dissolved Gas** (g.)			2 3	—	15.7	26.5	11.5	8.0

* Autoclave run series IV_A tabulated; Paraffin Oil III used.

** Condensed and dissolved gas found in the trap, cooled with alcohol and solid CO_2, connected to the autoclave.

*** The first 150 minutes at 350°C.

‡ Probably due to forcing out of the medium.

Table 4. Distillation Analysis* (Vol. %).

Temp. Range (°C.)	IV_A Ser. 124	IV_A Ser. 178	IV_A Ser. 82
<100	18.8	11.5	2.5
100–150	35.4	43.5	13.7
150–230	27.6	29.0	25.0
230–270	Began to crack at 216°C	—	13.4
270–300	—	—	12.2
Residue	10.8	—	24.0
Loss	7.4	—	9.2

* Made by Mr. O. Kamiike. The author takes this occasion to thank him for his co-operation.

Table 5. Effect on the Yield of Iso-butanol of Temperature.

Exp. No.	Vol. of Crude Isobutanol* (103–110°C.) (%)	Reaction Temp. (°C.)
IV_A Ser. 178	18	300–305
IV_A Ser. 124	16	330
IV_A Ser. 82	1.8	360

* Based on the total liquid condensates, exclusively of the condensates found in the trap.

alcohol and solid carbon dioxide). The presence of ethylene may be qualitatively accounted for by the results of Taylor and Van Hook[10] or of Farkas and Farkas[11] that the hydrogenation of acetylene to form ethylene is quite rapid and complete. The formations of butane and propane may be explained by the consideration of Egloff[12] that ethylene is the key molecule for the synthesis of hydrocarbons. He assigns to

Table 6. Gas Analysis*, **.

Temp. (°C.) and Exp. No.	300 178	330 139***	330 124	340 98	350 58 React.	350 58 Trap.	360 82 React.	360 82 Trap.
CO_2	0.2	3.3	0.0	0.3	0.0	29.8	0.3	4.2
C_2H_2	1.5	0.0	0.7	0.7	0.0	18.9	0.6	6.8
C_2H_4	3.0	0.3	1.2	1.0	3.0	17.3	1.7	22.0
C_nH_{2n}	0.8	0.0	1.1	0.2	0.3	0.0	0.4	3.0
O_2	0.4	0.4	0.3	0.5	0.5	0.0	0.9	0.4
CO	40.1	38.0	40.7	30.8	26.9	0.0	28.1	0.5
H_2	47.5	33.4	50.0	55.5	50.6	0.0	27.8	0.0
CH_4	3.7	2.1	4.3	6.5	15.4	0.0	34.1	0.0
N_2	2.8	2.5	1.7	3.5	2.3	0.0	6.1	1.8
C_3H_8	—	—	—	—	—	14.6	—	13.8
C_4H_{10}	—	—	—	—	—	18.7	—	47.1
Run No.	185	142	131	98	73		89	

* Since $CO:H_2$ varied for different runs, comparison cannot be quantitative.
** Approximately the middle run of each series taken.
*** No carbide is present.

the reaction, $2CH_2=CH_2 \rightarrow CH_3CH_2CH=CH_2$, which takes place quite readily according to various investigators[10][12][13], the activation energy of 35–37.7 kcal. per mole. In a closed system here employed, with excess of hydrogen, it is conceivable that the butylene thus formed is hydrogenated to butane. To account for the formation of propane, we shall

(10) H. A. Taylor and A. Van Hook, *J. Phys. Chem.*, **39**(1935), 811.
(11) A. Farkas and L. Farkas, *J. Am. Chem. Soc.*, **61**(1939), 3396. According to them, the activation energy is 12–17 kcal. on platinum surface, and according to Ref. (5), it is about 42 kcal./mol. in gas reaction.
(12) G. Egloff and E. Wilson, *Ind. Eng. Chem.*, **27**(1935), 917.
(13) Storch, *J. Am. Chem. Soc.*, **56**(1934), 374.

seek an additional explanation in the results of Storch[13] in which ethylene has been polymerized at 377°C and 141.5 mm. For the contact times less than 2 hours the formation of butene predominates, but for 3 hours that of propene becomes largest. He has explained the presence of the olefines with odd number of carbon atoms by assuming a disproportionation to give a higher and a lower olefine, taking one of his examples,

$$C_2H_4 + C_4H_8 \begin{cases} \nearrow 2C_3H_6 \\ \searrow C_6H_{12} \end{cases}.$$

It seems reasonable that this propene[14] is then hydrogenated to propane in our case.

The question as to whether ethane is present or not in these experiments made in liquid medium is, from our available data, not possible to be answered.

In our gas analysis the components of the saturated gases in a mixture have been calculated from the volume decrease and the volume of carbon dioxide produced after explosion. If the mixture contains more than two components, there will be a freedom of choice of any two components from the lot. This introduces uncertainty, as seems to be indicated by the results of the analysis of the gases found in the trap of IV_A Ser. 124 shown in Table 6B. Though there is this shortcoming in the method of analysis, it seems quite unlikely that it is a matter of chance that no ethane (or very slight) is found in the results of all the runs made in liquid medium while there is abundance of it in dry.

Table 6B. Analysis of Trap Gases for Autoclave Run IV_A Ser. 124.

Run No.	130	133	135
Gas			
CO_2	26.1	30.2	32.1
C_2H_2	12.9	16.2	18.2
C_2H_4	30.4	24.8	37.1
C_nH_{2n}	1.5	1.3	1.2
O_2	0.0	0.2	0.0
CO	3.1	2.8	0.8
H_2	0.0	0.8	0.3
CH_4	11.3	8.2	0.0
C_2H_6	14.6	14.4	0.0
C_3H_8	0.0	0.0	10.3

From theoretical considerations, however, the absence of ethane in excess of ethylene and hydrogen may not be entirely out of order. The following considerations are suggestive in this connection.

First, according to the work of Wood (quoted from Egloff[12]), the temperature for the initial appearance and the maximum formation of products in the thermal reactions of ethylene are as shown in Table 7.

Second, according to the results of Moore and Taylor[15], in their work on the mercury photosensitized hydrogenation of olefines, with about 40 mm. of olefine plus six fold excess of hydrogen, there is a significantly

(14) According to Ellis, "The Chemistry of Petroleum Derivatives," Vol. I, 80, The Chem. Catalog Co., Inc., N. Y., 1934, the results of Schneider and Frolich and of Lenher indicate that reactions of the type, $3C_2H_4=2C_3H_6$, e.g., the transformation of ethylene to propylene and not to butylene, can also take place although the mechanism of such reactions is still very obscure.

(15) W. J. Moore, Jr. and H. S. Taylor, *J. Chem. Phys.*, **8**(1940), 504.

Table 7.

Products	Temperature (°C.) Initial Appearance	Maximum Formation
C_4H_8, C_4H_6	350–400	650–750
C_2H_6	450–500	700
CH_4	500	1000
C_2H_2	650–700	1400
Aromatics	650	800–850

greater formation of propane and of butane from the respective olefines than that of ethane from ethylene. Their table is reproduced in Table 8.

Third, from the consideration of the energy of activation, it is of interest to note that the energy of activation of ethylene polymerization is less than that of hydrogenation, 35–37.7

Table 8.

Olefine Used	Olefine to Saturated Products (%) CH_4	C_2H_6	C_3H_8	C_4H_{10}	C_5H_{12}	C_6H_{14}	C_8H_{18}
C_2H_4	2	14	—	84	—	—	—
C_3H_6	2	1	26	5	2	64	—
C_4H_8	3	1	1	29	—	—	66

kcal./mole as against 43.2 to 51.5 kcal./mole[12] for the latter. Among ethylene, propylene, and butylene, the magnitude of the energy of activation of hydrogenation decreases with increasing molecular weight, as seen from the results obtained by Twigg[16] on the exchange and hydrogenation reactions between deuterium and the olefines on reduced nickel at 55–120°C. His results are given in Table 9. Toyama[17] and Kiyama[18] obtained a similar relative order of the activation energies of hydrogenation for the hydrogenation of ethylene, propylene, and isobutene also on reduced nickel at about the same temperature range.

Table 9.

Olefine	Activation Energy kcal./Mol.
Ethylene	8.2±0.5
Propylene	6.0
Butene-2	3.3
Isobutene	3.3

From what has been mentioned above, the absence of ethane in our experiments may not be out of harmony with the experimental facts already existing; but these considerations do not still completely explain why ethane is present in dry system while not in liquid medium[19].

(16) G. H. Twigg, *Trans. Faraday Soc.*, **35**(1939), 934.

(17) O. Toyama, *Rev. Phys. Chem. Japan*, **11**(1937), 353; **12**(1938), 115; **14**(1940), 86.

(18) R. Kiyama, *Rev. Phys. Chem. Japan*, **15**(1941), 137.

(19) Localization and accumulation of the heat of reaction in dry system may be the cause, but in lack of more definite evidence, this argument should not be pushed too strongly. The difference in the rates of polymerization in the two systems may not be entirely neglected from consideration.

Summary.

The synthesis of isobutyl alcohol in the presence of calcium carbide and a methanol catalyst has been made in liquid paraffin. It has been found that the reaction proceeds more smoothly, though not necessarily more effectively, than in dry system.

The effect of thorium on the catalytic activity of methanol catalyst has been investigated briefly. It has been found that 0.05 to 0.2 mole of it will increase the total yield of liquid products, but will not affect appreciably that of methanol.

The preponderate formations of ethylene, propane, and butane and the absence of ethane, even in the presence of excess ethylene and hyrogen, have been qualitatively explained.

The writer is grateful to Prof. T. Marusawa and to Dr. M. Sato for their interest and encouragement in this work. He is also grateful to Prof. H. Horiba for his comments on the paper prior to publication.

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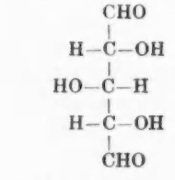
The Formation of Polyhydroxy-dialdehydes. III. *l*-Lyxo-trihydroxy-glutaric Dialdehyde and its Derivatives.

By **Koichi IWADARE.**

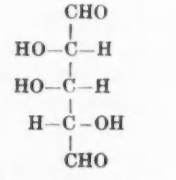
(Received June 8, 1942.)

Theoretically there should exist four dialdo-pentonoses, that is, trihydroxy-glutaric dialdehydes, and, among them, xylo- and *d*-lyxo-trihydroxy-glutaric dialdehydes (I and II) were reported in the first and second papers. This communication is concerned with the formation of *l*-lyxo-derivatives (or *l*-arabo-derivatives) (III).



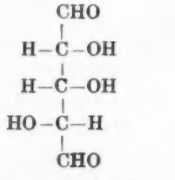
Xylo-trihydroxy-glutaric dialdehyde*

(I)



d-Lyxo-trihydroxy-glutaric dialdehyde*

(II)



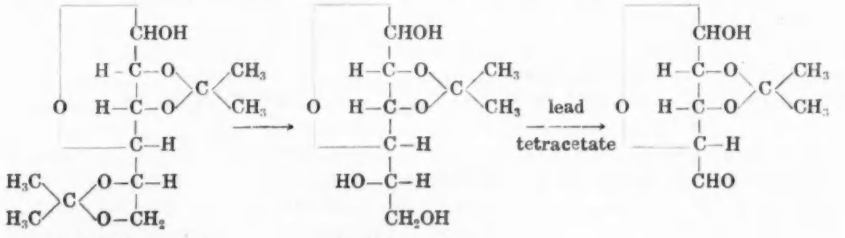
l-Lyxo-trihydroxy-glutaric dialdehyde*

(III)

(1) K. Iwadare, I, this Bulletin, **16**(1941), 40; II, *ibid.*, **16**(1941), 144.

* These formulas are described arbitrarily in chain.

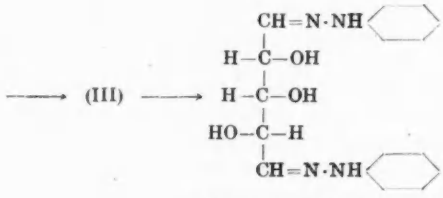
For obtaining *d*-lyxo-trihydroxy-glutaric dialdehyde, 2,3-monoacetone-*d*-mannofuranose was used as the starting substance, therefore it is plain that *l*-lyxo-trihydroxy-glutaric dialdehyde would be obtained from 2,3-monoacetone-*l*-mannofuranose. *l*-Mannose is obtained by cyanhydrin synthesis from *l*-arabinose[2], and shaken mechanically with acetone which contains a small quantity of concentrated sulphuric acid. 2,3,5,6-Diacetone-*l*-mannofuranose thus obtained crystallizes into colourless needles, m.p. 122°–122.5°, and has specific rotatory power, $[\alpha]_D$, of –27° in acetone. It is dissolved in biphthalate buffer solution (*p*H 4.4), and the solution is distilled by heating in an oil-bath at 140–150° for 1.5 hours, the necessary quantity of water being added during the distillation to keep the volume of the solution constant. Then the buffer solution containing diacetone-*l*-mannose and monoacetone-*l*-mannose which is obtained by partial hydrolysis of diacetone-derivative is neutralized (phenolphthalein) and evaporated to small volume under the diminished pressure, and extracted with ether for 72 hours. The ether extract is evaporated to thick sirup and thoroughly washed with boiling petroleum benzine to remove diacetone-mannose. The remaining sirup of 2,3-monoacetone-*l*-mannofuranose is dissolved in benzene and oxidized with lead tetracetate. The reaction mixture is filtered, the filtrate evaporated under the diminished pressure, and the remaining sirup is hydrolyzed by warming with dilute sulphuric acid. On adding phenylhydrazine to the solution, *bis*-phenylhydrazone of *l*-lyxo-trihydroxy-glutaric dialdehyde precipitates immediately. It is recrystallized from acetone on adding petroleum ether and then from alcohol. It crystallizes into colourless needles, m.p. 165–165.5° (corrected, decomposing). $[\alpha]_D = +73°$ in pyridine. *l*-Lyxo-trihydroxy-glutaric dialdehyde is obtained as sirup by decomposing the above-mentioned *bis*-phenylhydrazone with benzaldehyde. The specific rotation of this dialdehyde is calculated by directly measuring the rotation of its aqueous solution, which is obtained by decomposing the known quantity of its *bis*-phenylhydrazone, on the assumption that the conversion is quantitative. Thus, the specific rotatory power of *l*-lyxo-trihydroxy-glutaric dialdehyde, $[\alpha]_D^{10}$, is found to be –17°. *Bis*-*p*-nitro-phenylhydrazone of *l*-lyxo-trihydroxy-glutaric dialdehyde is obtained by adding the acidic aqueous solution of *p*-nitro-phenylhydrazine to the aqueous solution of the dialdehyde. Orange leaflets, m.p. 203.5–204° (decomposing).



2,3,5,6-Diacetone-*l*-mannofuranose (IV)

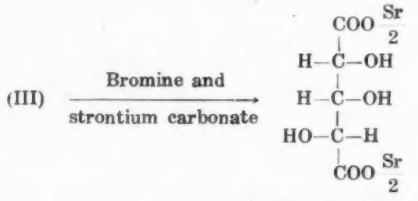
2,3-Monoacetone-*l*-mannofuranose (V)

(2) E. Fischer, *Ber.*, **23**(1890), 370; **24**(1891), 2683.



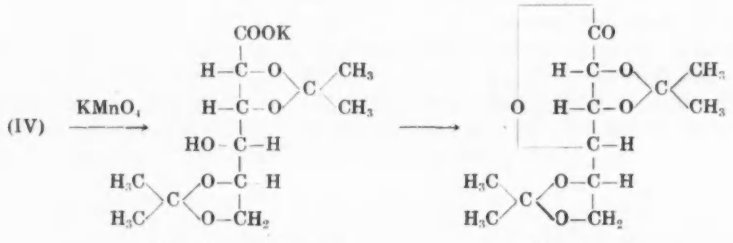
Bis-phenylhydrazone of *l*-lyxo-trihydroxy-glutaric dialdehyde*

By oxidizing the aldehyde groups of *l*-lyxo-trihydroxy-glutaric dialdehyde with bromine in the presence of strontium carbonate, strontium *l*-lyxo-trihydroxy glutarate is obtained.



Strontium *l*-lyxo-trihydroxy glutarate

By the way, diacetone-*l*-mannose is oxidized with potassium permanganate in alkaline solution, and potassium salt of diacetone-*l*-mannonic acid is obtained. This salt is converted into diacetone-*l*-mannonolactone, m.p. 124–124.5°, which agrees with that of *d*-isomer[3].



Potassium diacetone-*l*-mannonate

Diacetone-*l*-mannonolactone

Experimental. *2,3,5,6-Diacetone*-l-*mannofuranose.* Thirty grams of *l*-mannose, prepared from *l*-arabinose by cyanhydrin synthesis, were mechanically shaken for 6 hours with 1,200 c.c. of acetone containing 27 cc of concentrated sulphuric acid. The solution was neutralized with excess of anhydrous sodium carbonate and filtered. The filtrate, now coloured in light lemon-yellow, was concentrated to dryness under the

(3) Ohle and Berend, *Ber.*, **58**(1925), 2591.

diminished pressure. The crystalline residue was recrystallized from benzine. Yield, 28 g. It was recrystallized from ether by adding petroleum ether. Colourless needles, m.p. 122–122.5°. $[\alpha]_D=-27°$ in acetone (c=1.84). (Found: C, 55.49; H, 7.67. Calculated for $C_{12}H_{20}O_6$: C, 55.37; H, 7.73%).

*Monoacetone-*l*-mannofuranose.* Diacetone-*l*-mannose (5 g) was dissolved in 125 cc of biphthalate buffer solution of *p*H 4.4, and the mixture was distilled by heating in an oil-bath at 140–150° for 1.5 hours, the necessary quantity of water being added from time to time to maintain the initial volume. Then the solution was cooled, neutralized to phenolphthalein, evaporated to about 15 cc under the reduced pressure, and extracted continuously with ether for 72 hours. The ether extract was concentrated to sirup. In order to remove diacetone-derivative from the sirup, 30 cc of petroleum benzine (70–90°) was added to it, and the mixture was heated on a boiling water-bath, and stirred mechanically for 30 minutes. Benzine extract was removed by decantation, and the remaining sirup was again extracted with benzine just like as above. This procedure was repeated ten times and monoacetone-*l*-mannofuranose remained as sirup.

Bis-*phenylhydrazone of* l-*lyxo-trihydroxy-glutaric dialdehyde.* Benzene (30 cc) was added to monoacetone-*l*-mannose (1.4 g), the mixture was warmed at 60° and lead tetracetate (3 g) was added to it. After warmed 5 minutes, it was cooled, filtered and washed with acetone. The combined filtrate and washings were evaporated in vacuum to sirup. The remaining sirup was dissolved in 50 cc of N/20-sulphuric acid, and warmed on a water-bath for half an hour. It was evaporated in vacuum to remove the isolated acetone, filtered if necessary, and phenylhydrazine (2 g) was added to it. A considerable quantity of precipitate soon appeared from the mixture. It was filtered, dried, and dissolved in acetone. Acetone solution was filtered, if necessary, and *bis*-phenylhydrazone was precipitated by adding petroleum ether. It was recrystallized from alcohol into fine colourless needles, m.p., 165–165.5° (corrected, decomposing). $[\alpha]_D=+73°$ in pyridine (c=0.47). (Found: C, 62.41; H, 6.27; N 17.41. Calculated for $C_{17}H_{20}O_3N_4$: C, 62.18; H, 6.14; N. 17.06%).

l-*Lyxo-trihydroxy-glutaric dialdehyde.* The equilibrium rotatory power of *l*-lyxo-trihydroxy-glutaric dialdehyde was calculated from the rotatory power of its aqueous solution obtained by decomposition of the known quantity of its *bis*-phenylhydrazone. That is, 0.412 g of *bis*-phenylhydrazone was suspended in 6 cc of water and decomposed by benzaldehyde as mentioned above. The aqueous solution was made up to 10 cc by adding water and its rotatory power was measured with 1 dm tube. $\alpha_D=-0.32°$. As 0.186 g of free dialdehyde should be obtained from 0.412 g of its *bis*-phenylhydrazone, the specific rotatory power, $[\alpha]_D$, of *l*-lyxo-trihydroxy-glutaric dialdehyde is −17°.

Bis-p-*nitro-phenylhydrazone of* l-*lyxo-trihydroxy-glutaric dialdehyde.* Obtained just as d-isomer described in the previous paper[1], m.p., 203.5–204° (decomposing). (Found: N, 20.41. Calculated for $C_{17}H_{18}O_7N_6$: N, 20.09%).

Strontium l-*lyxo-trihydroxy-glutarate.* Obtained just as *d*-isomer described in the previous paper[1]. (Found: Sr, 33.34. Calculated for $C_6H_6O_7Sr$: Sr, 32.98%).

*Potassium salt of diacetone-*l*-mannonic acid.* Diacetone-*l*-mannose (1.5 g) was dissolved in 150 cc of water, and 0.33 g of potassium hydroxide and 0.65 g of potassium permanganate were added. After being kept on standing overnight, the mixture was filtered, the filtrate was neutralized with carbon dioxide, and evaporated under the reduced pressure. The residue was washed with ether and then extracted with cold alcohol. The alcohol extract was evaporated to small volume and ether was added to it. Fine needles appeared gradually. Yield, 1.25 g. They were recrystallized from acetone by adding benzene. $[\alpha]_D^{10}=+32.2°$ in water (c=1.34). (Found: K, 12.02. Calculated for $C_{12}H_{19}O_7K.H_2O$: K, 11.76%).

*Diacetone-*l*-mannonolactone.* Potassium salt of diacetone-*l*-mannonic acid (0.65 g) was dissolved in 2.2 cc of N-sulphuric acid, and the solution was at once extracted with ether. The ether extract was washed with water, dried wih anhydrous sodium sulphate, and evaporated in vacuum. The residue was crystallized from petroleum benzine into colourless needles. M.p., 124–124.5°. (Found: C, 55.68; H, 6.81. Calculated for $C_{12}H_{18}O_6$: C, 55.80; H, 7.02%).

Summary.

Following compounds were obtained in crystals: 2,3,5,6-Diacetone-*l*-mannofuranose, m.p., 122–122.5° and $[\alpha]_D=-27°$ (in acetone). *Bis*-phenylhydrazone of *l*-lyxo-trihydroxy-glutaric dialdehyde, m.p., 165–165.5° and $[\alpha]_D=+73°$ (in pyridine). *Bis-p*-nitro-phenyl-hydrazone of *l*-lyxo-trihydroxy-glutaric dialdehyde, m.p., 203.5–204°. Potassium diacetone-*l*-mannonate, $[\alpha]_D^{10}=+32.2°$ (in water). And diacetone-*l*-mannonolactone, m.p. 124–124.5°.

In conclusion the author wishes to express his hearty thanks to Prof. B. Kubota for his kind advice for this experiment.

Chemical Institute, Faculty of Science,
Imperial University of Tokyo.

Geochemische Untersuchungen der Vulkane in Japan. XXVII. Dichtemessungen der Solen aus Gas- und Petroleumbohrlöchern auf Taiwan (Formosa).

Von Shinya OANA.

(Eingegangen am 21. Mai 1942.)

Erdgase und Petroleum sprudeln aus Bohrlöchern manchmal mit Sole zusammen. Ich habe den Dichteunterschied zwischen den Solen aus Gas- und Petroleumbohrlöchern auf Taiwan und dem Standard-Leitungswasser mittels Schwimmermethode bestimmt. Diese Solen enthalten im allgemeinen Kohlenwasserstoffe. Diese werden beim gewöhnlichen Reinigungsprozesse nicht vollständig beseitigt. Dafür hat sich das folgende Verfahren bewährt: 100 ccm. Sole wird mit 10 g aktiver Kohle unter Rückflusskühler 30 Minuten lang gekocht. Nachdem die Sole bis auf Zimmertemperatur abgekühlt ist, wird die aktive Kohlen abfiltriert. Das Filtrat wird als Wasserdampf über Kupferoxyd, das auf 500°C. erhitzt ist, geleitet. Dadurch werden die Kohlenwasserstoffe vollständig beseitigt. Diese Probe wird dann nach dem gebräuchlichen Reinigungsprozesse weiter behandelt. Der Dichteunterschied gegen das Standard-Leitungswasser wird mittels Schwimmermethode bestimmt. Die gewonnenen Resultate sind in Tabelle 1 angegeben.

Tabelle 1. Dichteunterschied zwischen den Solen aus Gas- und Petroleumbohrlöchern auf Taiwan und dem Standard-Leitungswasser.

Bezeichnung der Bohrung	Ort		Tiefe, m
R 78 W	Pehtroleumbohrloch	Syukkōkō, Sintiku Provinz	957–1040
R 87 W	"	"	1202–1234
R 90 W	"	"	1113–1502
R 16 W	Gasbohrloch	Kinsui	1407
R 10 W	"	"	1438
R 8 W	"	Usiyama, Tainan-Provinz	714
R 6 W	"	Rokuzyūkei "	956

	Temperatur (°C)	Ergiebigkeit, hl/Tag	Cl^-, g/l	Dichteunterschied, γ
R 78 W	(15.5)	100.8	7.172	+ 0.6
R 87 W	(18.3)	12.0	7.794	+ 1.1
R 90 W	(45)	130.0	9.207	+ 2.0
R 16 W	—	—	0.3203	+ 0.6
R 10 W	26	21.8	14.20	+ 2.3
R 8 W	35	268	10.82	+ 3.5
R 6 W	55	4360	6.947	+ 3.8

Die eingeklammerten Temperaturen wurden an den Ausgängen der Bohrlöchern gemessen.

Dass die Behandlungen mit aktiver Kohle und Kupferoxyd die Isotopenverhältnisse des Wassers nicht ändern, ist in folgender Weise bestätigt worden. Drei Proben des gleichen Standard-Leitungswassers wurden nach obengenanntem Verfahren folgendermassen behandelt; die erste mit aktiver Kohle, die zweite mit Kupferoxyd, die dritte mit aktiver Kohle und danach auch mit Kupferoxyd. Die Dichteunterschiede zwischen diesen Proben und dem Standard-Leitungswasser wurden gemessen, nachdem sie dem gebräuchlichen Reinigungsprozesse entsphechend weiter behandelt worden waren. Die gewonnenen Resultat sind in Tabelle 2 angegeben.

Tabelle 2. Dichteunterschied zwischen drei verschieden behandelten Proben des Standard-Leitungswassers und dem unbehandelten Standard-Leitungswasser.

Ausgansprobe	Behandlung	Dichteunterschied, γ
Standard-Leitungswasser	aktive Kohle	− 0.0
"	Kupferoxyd	− 0.1
"	aktive Kohle und Kupferoxyd	− 0.1

Zum Vergleich habe ich auch Solen aus Petroleumbohrlöchern der japanischen Hauptinsel nach demselben Verfahren gereinigt, ihre Dichteunterschiede bestimmt und in Tabelle 3 zusammengestellt.

Tabelle 3. Dichteunterschied zwischen Solen aus Petroleumbohrlöchern der Hauptinsel und Standard-Leitungswasser.

Herkunft der Probe	Ort	Cl^-, g/l	Dichteunterschied, γ
Petroleumbohrloch	Takamati, Etigo-Provinz	7.597	+ 2.6
"	Haraiti, Kōduke-Provinz	13.04	+ 4.2
Mineralquelle*	Isobe, "	8.946	+ 2.4

* Die Mineralquelle von Isobe ist hier, obgleich sie keine Petroltumquelle ist, aufgeführt, weil sie in der nächsten Umgebung des Petroleumbohrlochs von Haraiti (etwa 2.1 km entfernt) entspringt.

Erörterung der Ergebnisse. Die Dichte der Solen aus Gas- und Petroleumbohrlöchern ist ausnahmslos höher als die Dichte des Standard-Leitungswassers. Wenn Proben benachbarter Herkunft in dieser Hinsicht miteinander verglichen werden, so ergibt sich eindeutig, dass die Wasserdichte mit der Chlorionenkonzentration steigt. Eine Ursache für Erhöhung der Konzentrationen der schweren Wasserisotopen im natürlichen Gewässer besteht in allmählicher Verdunstung des Wassers. Deshalb ergeben sich für Meerwasser und mineralisches Kristallwasser stark positive Dichtewerte. Dass die Dichteunterschiede der Solen aus Gas- und Petroleumbohrlöchern gross sind, deutet wohl auf Verdunstungsvorgänge oder auf Zusammenhänge zwischen Erdgas- und Petroleumvorkommen mit dem Meerwasser in geologischer Vorzeit hin. Schwere Wasserisotopen dürften danach ebenso wie Chloroionen oder andere Elemente durch Verdunstung konzentriert worden sein.

Es sei mir gestattet, Herrn Prof. Yuji Shibata und Herrn Prof. Kenjiro Kimura für ihre freundliche Anleitung und ihre Ratschläge, Herrn Toyojiro Ogura in dem Erdgas-Forschungsinstitut des Generalgouvernements von Taiwan für die liebenswürdige Überlassung der Proben und der Kaiserlichen Akademie der Wissenschaft für ihre finanzielle Unterstützung bei der Ausführung dieser Arbeit meinen herzlichen Dank auszusprechen.

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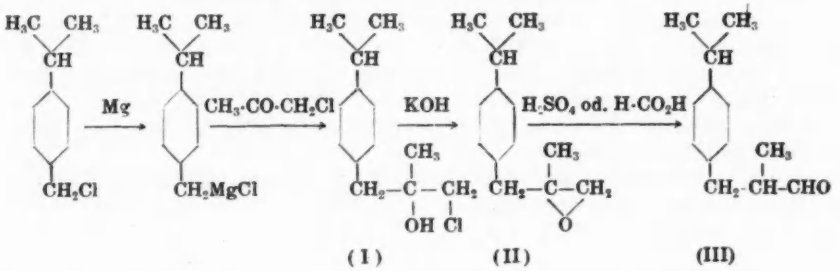
Synthese des *p*-Isopropyl-*α*-methylhydrozimtaldehyds.

Von **Masataro YAMASHITA** und **Tokiyoshi MATSUMURA.**

(Eingegangen am 17. Juni 1942.)

Vor kurzem[1] haben wir zwei verschiedenen Methoden zur Synthese des p-Isopropyl-*α*-methylhydrozimtaldehyds (sog. Cyclamenaldehyd), eines wichtigen synthetischen Riechstoffs, aus Cuminylchlorid veröffentlicht. Wie wir damals bemerkten, ist jedoch dieses Aldehyd schon früher von Knorr, Weissenborn[2] und Société des Usines Chimiques[3] synthetisiert worden.

Nuerdings haben uns auch die Synthese dieselben Aldehyds durch einen neuen Weg gelungen: Die durch Einwirkung von Mg auf Cuminylchlorid dargestellte Grignard-Verbindung wurde von Chloraceton in 2-Cuminyl-2-oxy-1-chlorpropan (I), dann von alkoholischer Kalilauge in 2-Cuminyl-2-methyläthylenoxyd (II) verwandelt. Schliesslich wurde das letzteres durch Schwefelsäure oder Ameisensäure zu dem Aldehyde (III) isomerisiert. Der oben erwähnte, von Verfassern aufgefundene Weg lässt sich folgendermassen veranschaulicht.



(1) M. Yamashita u. T. Matsumura, dies Bulletin, **16**(1941), 413.
(2) A. P. 1844013 (1932).
(3) F. P. 833644 (1938).

Beschreibung der Versuche. *2-Cuminyl-2-oxy-1-chlorpropan* (*I*). In einen Kolben, der mit einem Kühler versehen ist und in der sich eine Mischung aus 12.5 g. Mg-späne, einige Körnchen Jod und 300 ccm. Äther befindet, wurde allmählich eine Lösung von 85 g. (0.5 Mol) Cuminylchlorid (dargestellt aus Isopropylbenzol, Paraformaldehyd, Zinkchlorid und Salzsäure) in 300 ccm. absol. Äther zugesetzt. Nachdem sich die Grignard-Verbindung gebildet hat, versetzte man, unter Kühlung mit Eis-Kochsalzmischung auf $-5°$, tropfenweise mit einer Lösung von 46 g (0.5 Mol) Chloraceton in 50 ccm. Äther, was etwa 50 Min. beanspruchte. Zum Schluss liess man noch der Kolbeninhalt in Eis über Nacht stehen. Das Reaktionsgemisch wurde nun mit Eis und verd. Essigsäure zersetzt, die ätherische Lösung mehrmals mit Wasser gewaschen, mit Wasserfreiem Natriumsulfat getrocknet und man destillierte den Äther auf dem Wasserbad bei 50° ab. (I) bildet hellgelbes Öl. Ausbeute 94 g. Infolge Unbeständigkeit gegen Erhitzen wurde es, ohne gereinigt zu werden, weiter verarbeitet.

2-Cuminyl-2-methyläthylenoxyd (*II*). 44 g. Öl (I) in 100 g. 95 proz. Alkohol versetzte man, auf $-10°$ gekühlte, unter Rühren allmählich mit 25 proz. alkoholischer Kalilauge. Nach einstündigen Rühren neutralisierte man mit 10 proz. Essigsäure, filtrierte den Niederschlag ab und destillierte den Alkohol ab. Das zurückbleibende Öl wurde mit Äther verdünnt, getrocknet und fraktioniert. (1) 60–105° (3 mm.) 12 g. (2) 105–135° (3 mm.) 20 g. (3) der Rückstand 40 g.

Die (2) Fraktion, in welcher sich das gesuchte Oxyd befindet, wurde von neuem fraktioniert, wobei das Oxyd bei 111–113° (3 mm.) überging. Ausbeute 16 g. Es bildet hellgelbes Öl n_D^{15} 1.5094, d_4^{15} 0.9735, $[R_L]_D$ 58.39 (Berechnet für $C_{13}H_{18}O$: 58.08).

Diacetat.—Mit Essigsäureanhydrid acetyliert. Sdp. 153–156° (4 mm.). 1 g. Acetat: 20.60 ccm. N/2 KOH (Berechnet für $C_{13}H_{18}O_2(COCH_3)_2$: 20.99 ccm.

p-*Isopropyl-α-methylhydrozimtaldehyd* (*Cyclamenaldehyd*) (*III*). Nach dem man das Oxyd tropfenweise mit 60 g. 95 proz. Ameisensäure (od. mit 6N Schwefelsäure) versetzt hat, kochte man das Gemisch 2 Stunden im Ölbade. Das Reaktionsgemisch wurde mit Wasser und Äther geschüttelt, die Ätherschicht mit verd. Soda-Lösung, dann mit Wasser gewaschen und mit wasserfreiem Natriumsulfat getrocknet.

Die getrocknete Äther-Lösung wurde schliesslich fraktioniert. Cyclamenaldehyd ging bei 135–140° (10 mm.) über. Ausbeute 8 g. Es bildet hellgelbes Öl mit charakteristischem Geruch. Semicarbazon: Farblose Blättchen aus verd. Alkohol. Schmp. 169–170°. Mit dem von Verfassern früher[1] dargestellte Semicarbazon gemischt zeigt es keine Schmelzpunktserniedrigung.

Zum Schluss sind wir den Herrn S. Sawayama für seine Hilfe zu unseren besten Dank verpflichtet.

Laboratrium von Ogawa Chemische Industrie Aktiengesellschaft, Osaka, Japan.

Die Veränderung der chemischen Zusammensetzung der Thermalquellen unter dem Einfluss der Gezeiten.

Von Kazuo KURODA.

(Eingegangen am 23. Juni 1942.)

Einleitung.

Die Zusammenhänge zwischen den Thermalquellen und den Gezeiten sind von einigen Forschern bemerkt und vor allem vom geophysikalischen Standpunkt aus genau untersucht worden. Über die Veränderung der chemischen Zusammensetzung von Thermalquellen unter dem Einfluss von Ebbe und Flut sind jedoch bisher nur wenige Tatsachen bekannt, und wenn auch das Thermalwasser in seltenen Fällen analysiert wurde, so war die Analyse meist unvollkommen und ungenau. Keine Regelmässigkeiten in den Erscheinungen konnten bisher gefunden werden. Wir haben kürzlich die regelmässige Veränderung der Zusammensetzung der Thermalquellen von Ito, in der Provinz Sizuoka, beobachtet und ihre Abhängigkeit von Ebbe und Flut festgestellt. Die tägliche und zeitliche Veränderung ist erstaunlicherweise regelmässig und sehr gross. Wir fanden dabei eine unerwartete Tatsache: eine Thermalquelle hat ihre maximale Konzentration bei der Ebbe, ihre minimale Konzentration bei der Flut. Wir beabsichtigen ferner unsere Untersuchungen an anderen Thermalquellen, in verschiedenen Gegenden und bei verschiedenen Gezeitenverhältnissen vorzunehmen. Wir werden die Zusammenhänge zwischen See-, Grund-, und Thermalwasser klar zu machen, und ferner den Mechanismus der Thermalquellen zu erklären suchen. In dieser Abhandlung möchten wir jedoch die bis jetzt von uns erzielten Erbegnisse mitteilen.

Die Thermalquellen von Ito. Die Thermalquellen von Ito liegen an der östlichen Seeküste der Izu-Halbinsel. Sie sind sehr berühmt durch die grosse Zahl ihrer Quellen und ihre hohe Ergiebigkeit. Fukutomi und Fujii[1] haben im Jahre 1936 diese Thermalquellen geophysikalisch untersucht, und Temperatur, Ergiebigkeit, und Wasserniveau gemessen, sowie viele Quellen analysiert. Im Jahre 1940, hat T. Nakai[2] den Radiumgehalt der 20 Thermalquellen von Ito bestimmt und zeigt, dass die Radiumgehalte mit der Fukutomi'schen Theorie, nach der die Thermalquellen von Ito durch die Mischung von zwei verschiedenen Arten von Urthermalwasser und einem kalten Grundwasser gebildet werden, erklärt werden können. K. Okabe[3] hat kürzlich diese Quellen spektroskopisch analysiert und die Gegenwart von Silber und Gold in dem Thermalwasser nachgewiesen.

(1) K. Fukutomi und Z. Fujii, *Bull. Earthq. Res. Inst.*, **15**(1937), 506–535. K. Fukutomi, *Zisin*, **12**(1940), 404.
(2) T. Nakai, *dies Bulletin*, **15**(1940), 377.
(3) K. Okabe, Noch unveröffentlicht.

Die Gegenwart dieser Elemente ist nicht so unwahrscheinlich, da es in der Nachbarschaft von Ito einige Goldminen gibt. Okabe untersucht weiter die katalytische Wirkung dieser Thermalquellen. Einige Thermalquellen sind schon früh im Jahre 1889 vom chemisch-hygienischen Institut analysiert worden[4]. Die Radioaktivität wurde von R. Ishizu und Y. Kinugasa im Jahre 1913[4] und von dem Verfasser im März 1942 gemessen.

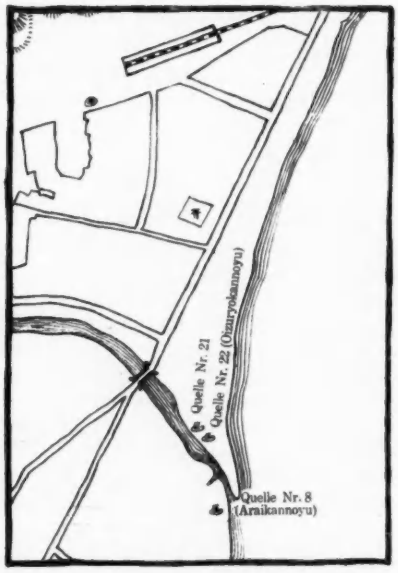


Abb. 1.

Analysenmethode. Eine hohe Genauigkeit der Analyse ist die notwendige Vorbedingung für unsere Untersuchung. Da eine grosse Zahl von Analysenresultaten notwendig ist, muss die Analysenmethode möglicht einfach und schnell sein. Die mühsame gravimetrische Methode ist unbrauchbar, wenn sie auch sehr genau ist. Wir haben deshalb hauptsächlich die volumetrische Methode angewandt.

(a) Temperaturmessung. Die Temperature wurde mit dem Maximum-Thermometer gemessen.

(b) *p*H-Messung. *p*H wurde kolorimetrisch mit Phenolrot als Indikator gemessen.

(c) Ergilbigkeitsmessung. Die Zeit, die zur Füllung eines 8 l-Eimers notwendig war, wurde gemessen.

(d) Atmosphärendruck. Mit einem Barometer gemessen.

(e) Abdampfrückstandbestimmung. 100 ccm Thermalwasser auf einem Wasserbad abgedampft, 1 Stunde bei 110°C getrocknet, und gewogen.

(f) Chlor. Zu 20 ccm Wasserprobe wurden 0.5 ccm K_2CrO_4 Lösung (10%ig) addiert, und mit N/10 $AgNO_3$ Lösung titriert. N/10 $AgNO_3$ Lösung: 16.9888 g $AgNO_3$ in 1 Liter Wasser gelöst. 1 ccm von dieser Lösung entspricht 3.5457 mg Cl'.

(g) Sulfat. Zu 100 ccm Wasserprobe wurde Benzidinhydrochloridlösung addiert, 5 Minuten mit einem Rührstock gerührt, durch 5A Toyo-Filterpapier filtriert, 2 mal mit je 10 ccm kaltem Wasser gewaschen. Der Niederschlag von Benzidinsulfat und das Filterpapier wurden in einen Becher gebracht, 100 ccm Wasser addiert, bis 60°C erwärmt, und nach Zusatz von etwa 2 ml Phenolphthaleinlösung mit N/10 NaOH bis zur bleibenden Rotfärbung titriert.

(4) R. Ishizu, "The Mineral Springs of Japan," 71, Tokyo (1915).

Benzidinlösung:[5] Zur Herstellung der Benzidinlösung löst man 6.7 g reine Benzidinbase in 20 ml HCl(D=1.12) und verdünnt mit Wasser zu 1 Liter.

(h) Bestimmung von Calcium. Zu 50 ccm Wasserprobe addiert man 5 ccm NH_4OH (5:95) und kocht die Lösung. 10 ccm Ammoniumoxalatlösung (gesättigt) wurde addiert und 3 Minuten gekocht, 1 Stunde stehen gelassen und filtriert. Der Niederschlag wurde mit kaltem Wasser 5 mal gewaschen, dann in 20–30 ccm heissem H_2SO_4(1:3) gelöst, und bei 60–70°C. mit N/10 $KMnO_4$ Lösung titriert.

1 ccm N/10 $KMnO_4$ Lösung entspricht 2.004 mg. Ca.

(i) Bestimmung von Natrium. (a) Volumetrische Methode[6]. 10 ccm Wasserprobe wurden vorsichtig bis auf 5 ccm abgedampft. 35 ccm Zink-Uranyl-Acetat Reagens addiert. 5 Min. gerührt, 1 Stunde stehen gelassen und durch ein Glasfilter filtriert. Sodann 4 mal mit je 2 ccm absolutem Alkohol gesättigt mit dem Niederschlag von $Zn{\cdot}Na{\cdot}(UO_2)_3(C_2H_3O_2)_9$ gewaschen. Der Niederschlag wurde in 100 ccm Wasser gelöst und mit N/2 NaOH bis Rotfärbung von Phenolphthalein eintrat, titriert. Dann wurde die Lösung gekocht, und wenn die Lösung farblos geworden, 5 ccm N/2 NaOH addiert und 5 Min. gekocht. Diese Operation wurde wiederholt bis zur bleibenden Rotfärbung. Dann titriert man den Basenüberschuss mit N/2 HCl. Die Reaktion verläuft wie folgt:

$$NaZn(UO_2)_3(Ac)_9 + 10\,OH^- \rightarrow Na^+ + Zn\,UO_4 + U_2O_7^{--} + 9\,Ac^- + 5\,H_2O$$

Wir müssen zuerst die Beziehung zwischen der Natriummenge und dem Volumen der N/2 NaOH Lösung mittels Natriumchlorid Normallösung feststellen. (b) Gravimetrische Methode[7]. Obenerwähnte volumetrische Methode ist jedoch nicht so genau. Wenn eine hohe Genauigkeit der Analyse erwünscht ist, müssen wir die gravimetrische Methode anwenden.

Der Niederschlag von $Zn{\cdot}Na{\cdot}(UO_2)_9$ Acetat wurde durch ein Glasfilter filtriert, mit Alkohol gewaschen, bei 110°C. 30 Min. getrocknet und gewogen.

Experimentalresultat.

l. Zeitliche Veränderung des Chlorgehaltes der Quelle Nr. 13 (Araikannoyu) am 15. März, 1942.

Die Quelle Nr. 13 liegt sehr nahe an der Seeküste (ungefähr 50 m). in der Nähe des Ufers des Ito-Okawa Flusses.

Die Quelle ist 90.90 m. tief. Sie wurde im Jahre 1919 ausgebaut. Der Besitzer sagt, dass diese Thermalquelle beträchtlich durch Ebbe und Flut beeinflusst wird.

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(5) Kurtenacker, "Analytische Chemie der Sauerstoffsäuren des Schwefels," 24, Stuttgart (1938).

(6) Dobbins und Byrd, *J. Am. Chem. Soc.*, **53**(1931), 3288.

(7) Caley und Foulk, *J. Am. Chem. Soc.*, **51**(1929), 1664.

Der Verfasser war am 15. März 1942 in Ito gewesen, und hat je 1 Stunde, Temperatur und Chlorgehalt dieser Quelle gemessen. Das Resultat ist in Tabelle 1 angegeben (Tabelle 1).

Tabelle 1. Quelle Nr. 13.
15. März 1942.

Zeit	Temp. der Quelle °C	Cl′ (g/L)
10_h. 10	41.5	1.4410
11_h. 10	41.5	1.4374
12_h. 10	41.5	1.4566
13_h. 5	41.7	1.4717
14_h. 5	41.7	1.4916
15_h. 5	41.5	1.5178

Tabelle 2.

Flut		Ebbe	
Zeit	Niveau (cm)	Zeit	Niveau (cm)
4_h. 15	138	10_h. 00	59
15_h. 45	138	22_h. 25	14

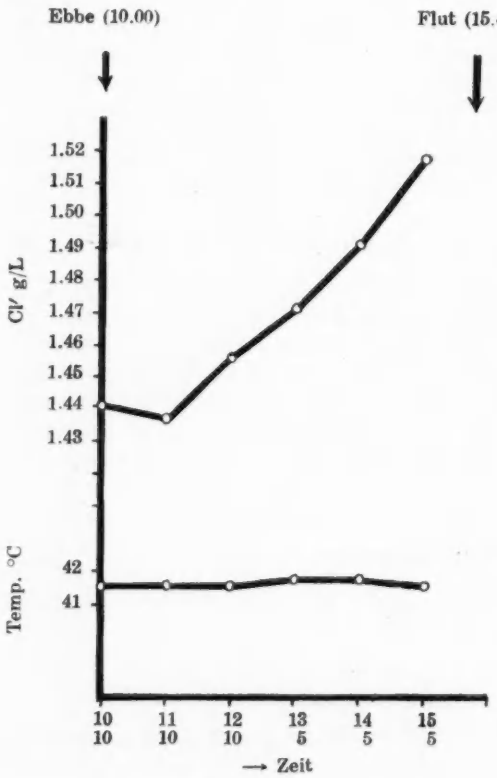

Abb. 2. Quelle Nr. 13. 15. März 1942.

Die Temperatur bleibt beinahe konstant, der Chlorgehalt vergrössert sich indes merkwürdigerweise regelmässig. Die Zeit von Ebbe und Flut in Ito war am 15. März 1942, wie folgt (Tabelle 2).

Wie man aus Abb. 2 ersieht, gehen Niveau und Chlorgehalt parallel zueinander. Es kann nicht bezweifelt werden, dass die regelmässige Veränderung des Chlorgehalts dieser Quelle von Ebbe und Flut verursacht wird. Die Experimente wurden leider nicht lange fortgesetzt, so dass wir das Resultat nicht ausführlich diskutieren können.

II. Zeitliche Veränderung des Chlorgehaltes der Quelle Nr. 13 (Araikannoyu) am 30. März 1942.

Am. 30. März 1942 wurden wieder die Chlorbestimmung, Temperatur- und *p*H Messung durchgeführt. Das Resultat war sehr ähnlich wie am 15. März 1942. (Tabelle 3).

Wie man aus Abb. 3 ersieht, wird das Niveaumaximum um 15_h 20 erreicht, um 16_h 00 zeigt sich jedoch ein höherer Gehalt an Chlor als um

15_h 00. Der Zusammenhang zwischen Niveau und Chlorgehalt scheint etwas verschoben.

Tabelle 3. Quelle Nr. 13.
30. März 1942.

Zeit	Temp. der Quelle °C (Lufttemperatur °C)	*p*H	Cl′ (g/L)
13_h. 00	41.5(18.3)	7.45	1.4339
14_h. 00	41.5(19.1)	7.45	1.4522
15_h. 00	41.6(19.0)	7.45	1.4636
16_h. 00	— (—)	7.45	1.4771

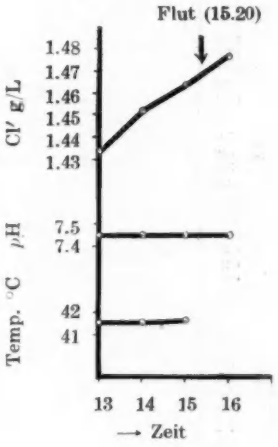

Abb. 3. Quelle Nr. 13.
30. März 1942.

III. Zeitliche Veränderung der chemischen Zusammensetzung der Quelle Nr. 21 von 30. bis 31. März 1942.

Diese Quelle liegt an der anderen Seite des „Ito-Okawa", ungefähr 100 m von der Seeküste entfernt.

Ort der Quelle: 178–18, Kuzumihara, Matubara, Ito, Takata-Gun. Sizuoka-Ken (Provinz Sizuoka).

Besitzer: Herr T. Kitamura.

Verwalter: Herr M. Saito.

Tiefe der Quelle: 205.5 m (bis 52 m Eisenrohr).

Die Quelle soll beträchtlich von Ebbe und Flut beeinflusst werden. Die Quelle wird auch von dem Niveau des Flusswassers beeinflusst.

Tabelle 4.

	Flut		Ebbe	
	Zeit	Niveau (cm)	Zeit	Niveau (cm)
30. März	3_h. 35	138	9_h. 35	51
"	15_h. 20	137	21_h. 55	20
31. März	4_h. 5	143	10_h. 10	36
"	16_h. 15	147	21_h. 35	19

Wir haben vom 30. bis 31. März 1942, 24 Stunden an dieser Quelle, Temperatur, *p*H, Ergiebigkeit, Cl′, SO''_4, Na′, und Ca″ gemessen.

Die Zeit von Ebbe und Flut in Ito am 30.–31. März 1942 war, wie folgt (Tabelle 4):

Das Resultat ist in Tabelle 5 und in Abb. 4 angegeben.

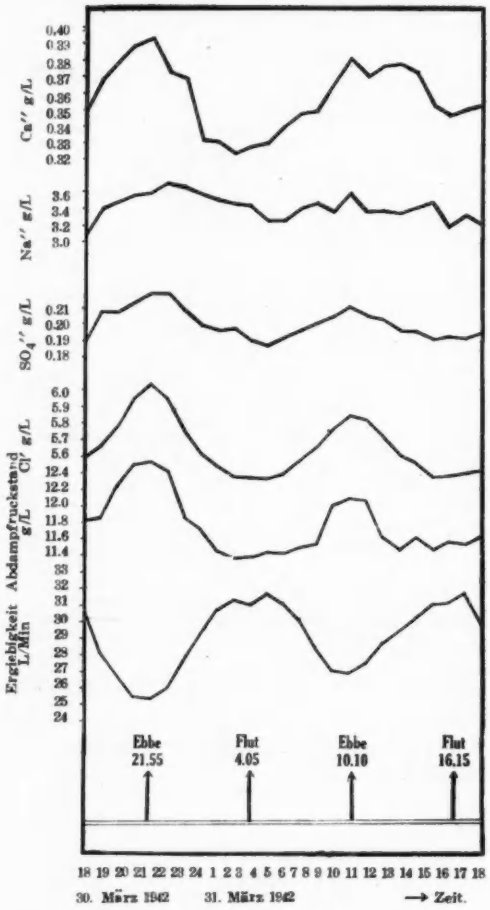

Abb. 4. Quelle Nr. 21. 30-31. März 1942.

Die Beziehung ist in diesem Fall ganz merkwürdig. Niveau und Ergiebigkeit verlauften ganz parallel, Cl', SO_4'', $Na^{\cdot}$, $Ca^{\cdot\cdot}$ usw. verändern sich jedoch umgekehrt. Die maxima von Cl', SO_4', $Na^{\cdot}$, $Ca^{\cdot\cdot}$, usw. stimmen mit den Minima von Niveau und Ergiebigkeit überein.

IV. Zeitliche Veränderung der chemischen Zusammensetzung der Quelle Nr. 21 vom 24. bis 25. April 1942.

Wir haben vom 24.–25. April 1942, d.h. in einer Halbmondnacht, bei dieser Quelle wieder dasselbe Experiment durchgeführt. Es wurde erwartet, dass in dieser Nacht das Niveau beinahe konstant und dementsprechend die Zusammensetzungsänderung auch nicht so gross ist. Das Resultat entsprach unserer Erwartung. Die Veränderungen von Temperatur, *p*H, Ergiebigkeit, Chlor, und Sulfat sind sehr gering, Maxima von Chlorgehalt traten zweimal auf, am 24. April um 17_h und am 25. April um 7_h, Minima traten ebenfalls zweimal auf, am 24. April um 9_h (Flut Zeit 9.20) und am 25. April um 2_h (Flut-Zeit 0.45). Die Veränderung des Sulfates war nicht sehr regelmässig, weil die Analysenmethode von Sulfat nicht so genaue Messungen ermöglicht wie bei Chlor. Wir konnten daher bei dem Sulfatgehalt die zu erwartenden kleinen Veränderungen nicht feststellen. Die Neigung scheint jedoch ähnlich zu sein. Die Ergiebigkeit war ebenfalls etwas unregelmässig.

Die Zeit von Ebbe und Flut in Ito am 24.–25. April 1932 war, wie folgt (Tabelle 6).

V. Zeitliche Veränderung der chemischen Zusammensetzung der Quelle Nr. 22. (Oizuryokannoyu) vom 24. bis 25. April 1942.

Diese Quelle sprudelt ganz in der Nähe der Quelle Nr. 21, jedoch näher der Küste. Die Quelle ist auch ungefähr 100 m von der Seeküste entfernt. Tiefe der Quelle: 156 m (Eisenrohr 73 m).

Tabelle 5. Quelle Nr. 21. 30–31 März 1942.

Zeit	Luft-temp. (°C)	Temp. der Quelle (°C)	pH	Er-giebig-keit (L/Min)	Ab-dampf-rück-stand (g/L)	Cl' (g/L)	SO_4'' (g/L)	$Na^{\cdot}$ (g/L)	$Ca^{\cdot\cdot}$ (g/L)	
$18_h.$ 00	17.0	45.0	7.3	33.5	11.80	5.582	1.890	3.09	0.3486	
$19_h.$ 00	16.4	45.0	7.2	28.2	11.84	5.659	2.070	3.41	0.3667	
$20_h.$ 00	17.6	45.0	7.3	25.7	12.22	5.780	2.061	3.48	0.3783	
$21_h.$ 00	16.0	45.0	7.3	23.0	12.48	5.954	2.122	3.57	0.3880	
$22_h.$ 00	15.5	45.0	7.4	22.8	12.52	6.032	2.171	3.59	0.3923	← **Ebbe (21.55)**
$23_h.$ 00	14.7	45.0	7.3	24.0	12.40	5.936	2.180	3.72	0.3711	
$24_h.$ 00	14.2	45.0	7.3	27.7	11.85	5.748	2.072	3.68	0.3680	
$1_h.$ 00	13.7	45.0	7.3	30.6	11.71	5.610	1.982	3.59	0.3305	
$2_h.$ 00	13.1	45.0	7.3	33.6	11.44	5.535	1.951	3.52	0.3293	
$3_h.$ 00	12.7	45.0	7.3	34.8	11.37	5.475	1.965	3.47	0.3229	
$4_h.$ 00	12.7	45.0	7.3	34.2	11.38	5.464	1.893	3.45	0.3265	← **Flut (4.05)**
$5_h.$ 00	12.2	44.9	7.3	35.5	11.43	5.461	1.863	3.26	0.3285	
$6_h.$ 00	12.3	44.9	7.3	34.2	11.42	5.489	1.916	3.26	0.3386	
$7_h.$ 00	12.5	45.0	7.3	32.4	11.49	5.578	1.960	3.41	0.3466	
$8_h.$ 00	12.4	45.0	7.3	29.0	11.53	5.656	2.005	3.48	0.3474	
$9_h.$ 00	13.5	45.0	7.3	26.2	12.02	5.762	2.042	3.37	0.3659	
$10_h.$ 00	15.0	45.0	7.3	25.9	12.09	5.840	2.100	3.59	0.3763	← **Ebbe (10.10)**
$11_h.$ 00	15.1	45.0	7.4	27.0	12.06	5.815	2.048	3.37	0.3695	
$12_h.$ 00	13.8	45.0	7.4	29.5	11.60	5.713	2.029	3.38	0.3759	
$13_h.$ 00	12.0	45.0	7.3	30.9	11.44	5.606	1.952	3.35	0.3769	
$14_h.$ 00	11.9	45.0	7.3	32.5	11.60	5.557	1.948	3.42	0.3614	
$15_h.$ 00	17.7	45.0	7.3	34.3	11.44	5.472	1.900	3.50	0.3514	
$16_h.$ 00	17.0	45.0	7.3	34.3	11.55	5.479	1.912	3.19	0.3458	← **Flut (16.15)**
$17_h.$ 00	15.8	45.0	7.3	35.5	11.53	5.493	1.905	3.33	0.3498	
$18_h.$ 00	14.0	45.0	7.3	32.0	11.61	5.514	1.942	3.21	0.3522	

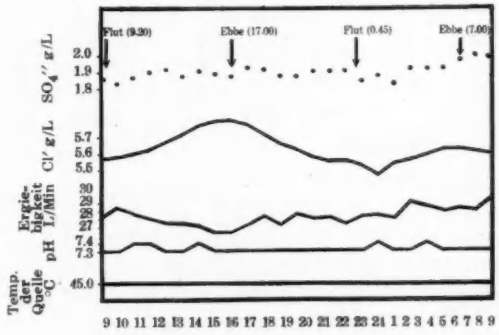

Abb. 5. Quelle Nr. 21. 24.–25. April 1942.

Tabelle 6.

	Flut	
	Zeit	Niveau (cm)
24. April	9.20	105
25. April	0.45	120
	11.40	103
	Ebbe	
	Zeit	Niveau (cm)
24. April	5.00	94
	17.00	45
25. April	7.00	86
	18.35	47

Das Experimentalresultat ist in Tabelle 8 angegeben. Die Neigung war ganz dieselbe wie bei Quelle No. 21. Die Veränderung war jedoch etwas kleiner. Die Ursache dafür ist vielleicht darin zu suchen, dass diese Quelle ein längeres Eisenrohr als die Quelle Nr. 21 hat. Die Quelle sprudelt unter der Badeanstalt hervor, die Probeentnahme war infolgedessen sehr schwer. Wir haben deshalb die Temperatur in der Badeanstalt

Tabelle 7. Quelle Nr. 21. 24–25. April 1942.

Zeit	Luft-Temperatur (°C)	Luftdruck (mm)	Temp. der Quelle (°C)	*p*H	Ergiebigkeit (L/Min)	Cl′ (g/L)	SO_4'' (g/L)	
9_h. 00	18.5	760	45.0	7.3	28.2	5.567	1.857	← **Flut (9.20)**
10_h. 00	19.5	760	45.0	7.3	29.4	5.575	1.830	
11_h. 00	22.1	758	45.0	7.4	28.7	5.590	1.868	
12_h. 00	23.0	758	45.0	7.4	28.1	5.613	1.900	
13_h. 00	23.4	758	45.0	7.3	27.6	5.669	1.915	
14_h. 00	23.7	758	45.0	7.3	27.7	5.707	1.872	
15_h. 00	22.1	757	45.0	7.4	27.4	5.760	1.905	
16_h. 00	24.0	757	45.0	7.3	26.5	5.790	1.888	
17_h. 00	21.8	757	45.0	7.3	26.4	5.798	1.875	← **Ebbe (17.00)**
18_h. 00	19.2	757	45.0	7.3	27.3	5.772	1.922	
19_h. 00	15.0	758	45.0	7.3	28.4	5.707	1.913	
20_h. 00	12.1	758	45.0	7.3	27.3	5.650	1.871	
21_h. 00	12.8	757.5	45.0	7.3	28.6	5.613	1.871	
22_h. 00	11.1	757.5	45.0	7.3	28.0	5.567	1.904	
23_h. 00	10.3	758	45.0	7.3	28.2	5.541	1.902	
24_h. 00	9.5	758	45.0	7.3	27.4	5.544	1.901	
1_h. 00	9.5	759	45.0	7.3	28.4	5.514	1.845	← **Flut (0.45)**
2_h. 00	8.8	758	45.0	7.4	28.6	5.465	1.878	
3_h. 00	8.3	758	45.0	7.3	28.1	5.533	1.829	
4_h. 00	8.2	758.5	45.0	7.3	30.0	5.556	1.911	
5_h. 00	8.0	758.5	45.0	7.4	29.5	5.582	1.919	
6_h. 00	9.7	759	45.0	7.3	28.9	5.613	1.920	
7_h. 00	13.0	759	45.0	7.3	29.3	5.620	1.978	← **Ebbe (7.00)**
8_h. 00	18.3	759	45.0	7.3	29.1	5.605	2.000	
9_h. 00	21.3	759	45.0	7.3	30.6	5.598	1.991	

Tabelle 8. Quelle Nr. 22. 24–25. April 1942.

Zeit	Temp. der Quelle (°C)	*p*H	Cl′ (g/L)	
9_h 20	45.0	7.5	4.744	← **Flut (9.20)**
10_h. 30	45.0	7.5	4.733	
11_h. 30	45.0	7.5	4.748	
12_h. 30	45.0	7.5	4.752	
13_h. 30	45.0	7.6	4.752	
14_h. 30	45.0	7.5	4.793	
15_h. 30	45.1	7.5	4.793	
16_h. 30	45.1	7.5	4.797	← **Ebbe (17.00)**
17_h. 30	45.1	7.6	4.786	
18_h. 30	45.0	7.6	4.759	
19_h. 30	45.0	7.6	4.759	
20_h. 30	45.0	7.6	4.733	
21_h. 30	45.0	7.5	4.729	

gemessen. Hier fanden wir eine um 1°C. niedriger liegende Temperatur. Die richtige Temperatur der Quelle liegt also mit 46°C., etwas höher als die der Quelle Nr. 21.

Diskussion. K. Honda und T. Terada[8] bemerkten bei den Thermalquellen von Atami schon im Jahre 1906 eine regelmässige Hebung und Senkung des Wasserniveaus. Eine Thermalquelle, die in der Nähe der Oyu-Quelle (Geiser) liegt, verändert ihr

(8) K. Honda und T. Terada, Publications of the Earthquake Investigation Committee No. **22A** (1906), 51.

Tabelle 8.—(*Fortsetzung*)

Zeit	Temp. der Quelle (°C)	*p*H	Cl′ (g/L)	
22_h. 30	45.0	7.5	4.714	
23_h. 30	45.0	7.6	4.710	
24_h. 30	45.0	7.5	4.695	← **Flut (0.45)**
1_h. 30	45.0	7.5	4.684	
2_h. 30	45.0	7.6	4.702	
3_h. 30	45.0	7.5	4.695	
4_h. 30	45.0	7.5	4.695	
5_h. 30	45.0	7.5	4.718	
6_h. 30	45.0	7.5	4.736	← **Ebbe (7.00)**
7_h. 30	45.0	7.6	4.740	
8_h. 30	45.0	7.6	4.729	
9_h. 30	45.1	7.7	4.721	

Niveau unter dem Einfluss des Geisers, und ein Thermalquelle, die in der Nähe der Seeküste liegt, unter dem Einfluss von Ebbe und Flut. Obige Autoren haben jedoch gar nichts über die Veränderung der chemischen Zusammensetzung der Thermalquellen geschrieben. R. Nomitu[10] hat bei den Thermalquellen von Beppu in der Provinz Oita den Einfluss der Gezeiten auf die Thermalquellen studiert. Er schreibt, dass die Ergiebigkeit sich parallel zu Ebbe und Flut verändert, die elektrische Leitfähigkeit der Thermalquellen aber genau umgekehrt ist. Dies ist eine sehr interessante Erscheinung, die wir chemisch noch einmal genau studieren müssen. K. Maeda[9] hat bei den Thermalquellen von Asamusi in der Provinz Aomori diese Erscheinung wieder vom geophysikalischen Standpunkt aus genau untersucht. Er schreibt über die Veränderung des Chlorgehalts nur sehr kurz wie folgt: „Der Chlorgehalt der Thermalquellen wurde bestimmt, genügende Ergebnisse konnten jedoch noch nicht erzielt werden."

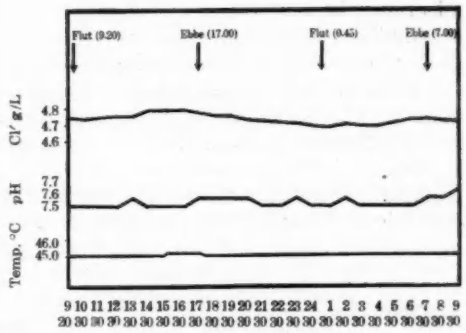

Abb. 6. Quelle Nr. 22. 24.–25. April 1942.

Fukutomi hat vom 5.–26. November 1937 siebzehn Thermalquellen in Ito untersucht. Er schreibt in seiner Mitteilung wie folgt:[1] „Die Ergiebigkeit der Thermalquellen von Ito verändert sich, die Temperatur und der Chlorgehalt aber bleibt immer beinahe konstant". In seiner Abhandlung über die Thermalquellen von Yatu schreibt Fukutomi wieder wie folgt[10]: „Die Veränderung der Ergiebigkeit der Thermalquellen von Yatu beträgt 2/3 der Ergibigkeit des Durchschnittsniveaus der Gezeiten. Die Temperatur und der Chlorgehalt ändert sich jedoch nur um 1/30. Wir können daher daraus schliessen, dass die Temperatur und der Chlorgehalt immer konstant war. Dies ist eine bemerkenswerte Erscheinung, und wir möchten annehmen, dass der Einfluss von Ebbe und Flut auf die Ther-

(9) K. Maeda, *Zisin*, **8**(1936), 1.
(10) Fukutomi, *Zisin*, **8**(1936), 457.

malquellen nicht durch die Mischung von Seewasser und Thermalwasser verursacht wird, sondern nur der Veränderung des Gezeitendrucks auf den Wasserdruck im Thermalquellenwasserweg zuzuschreiben ist". Meine neue Untersuchung zeigt jedoch, dass diese Fukutomi'sche Theorie nicht immer gültig ist. Meine Ergebnisse können nicht erklärt werden, ohne die Mischung von Thermalwasser und anderem Wasser in Betracht zu ziehen. Die Veränderung des Chlorgehaltes der Quelle Nr. 13 (Araikannoyu) kann durch die Mischung von Seewasser und Thermalwasser leicht erklärt werden. Die regelmässige Veränderung der chemischen Zusammensetzung der Quelle Nr. 21 ist jedoch etwas schwer zu erklären. Die maximale Ergiebigkeit und minimale Konzentration stimmen immer überein. Es ist kaum anzunehmen, dass diese Erscheinung durch die Verzögerung des Einflusses der Gezeiten verursacht wird. Wir müssen also die Vermischung mit Grundwasser berücksichtigen. Dasselbe ist weit stärker verdünnt als das See- und Thermalwasser. Seine Temperatur ist uns noch nicht bekannt.

Weil die Temperaturveränderung jedoch immer weniger als 0.1°C. betrug, müssen wir daraus schliessen, dass die Mischung schon in der Tiefe geschieht oder dass die Temperatur des Grundwassers und des Thermalwassers ganz gleich war. In letzteren Fall, können wir die Vermischung in der Nähe der Erdoberfläche vermuten. Wir können dies schematisch darstellen (s. Abb. 7). Das Grundwasser stromt durch ein in der Nähe der Erdoberfläche liegendes Loch in das Eisenrohr ein. Bei der Ebbe ist das Niveau des Grundwassers unter diesem Loch, bei der Flut über diesem Loch. Es ist indes unwahrscheinlich, dass es in der Nähe der Erdoberfläche ein Loch in dem Rohr gibt, und dort die Temperatur des Grund- und Thermalwassers gleich ist. Es ist viel wahrscheinlicher und leichter zu erklären, dass die Vermischung in der Tiefe geschieht. Ein derartiges Modell wird in Abb. 8 gezeigt. In diesem Fall wirkt das

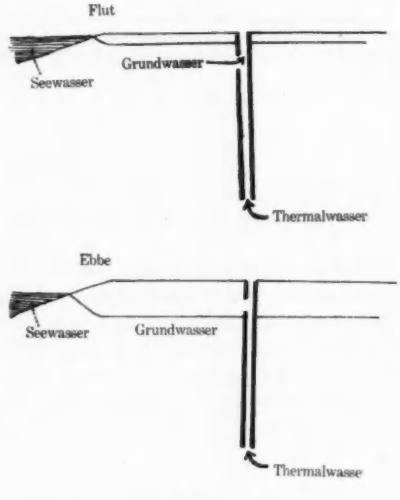

Abb. 7.

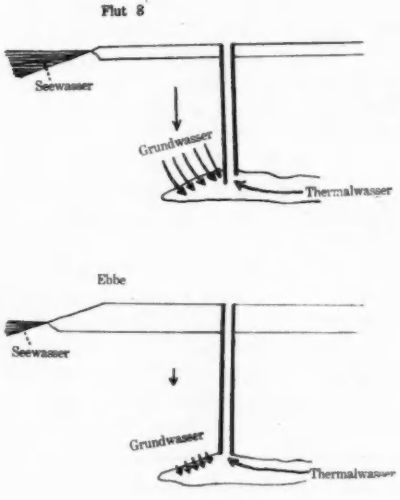

Abb. 8.

Seewasser nur druckgebend, d.h. das Seewasser fliesst gar nicht in das Thermalwasser ein, sondern drückt nur das Grundwasser ins Thermalwasser. Bei der Flut erreicht dieser Druck ein Maximum und die grösste Menge von verdünntem Grundwasser fliesst in das Thermalwasser; deshalb hat die Thermalquelle ihre minimale Konzentration bei der Flut. Der Druck erreicht sein Minimum bei der Ebbe, aus diesem Grunde ist auch die in die Thermalquelle fliessende Grundwassermenge am geringsten; deshalb hat die Thermalquelle ihre maximale Konzentration bei der Ebbe.

Um diese Ansicht zu bestätigen, ist die Temperaturmessung in der Tiefe des Thermalquellenrohrs notwendig. Der Verfasser hat den Plan, die Temperatur mit einem Widerstandthermometer zu messen. Die Ergebnisse seiner Experimente werden später berichtet werden.

Zusammenfassung.

(1) Die Veränderung der chemischen Zusammensetzung der Thermalquellen von Ito unter dem Einfluss der Gezeiten wurde untersucht.

(2) Die zeitliche Veränderung der chemischen Zusammensetzung einiger Thermalquellen von Ito ist erstanunlicherweise gross und regelmässig.

(3) Die Thermalquelle Nr. 21 hat ihre maximale Konzentration bei der Ebbe und ihre minimale Konzentration bei der Flut.

(4) Diese Erscheinungen können nicht erklärt werden, ohne die Vermischung von Thermalwasser mit anderem Wasser in Betracht zu ziehen. Wir müssen die Vermischung mit Grundwasser berücksichtigen.

Ich erlaube mir hiermit Herrn Prof. Kenjiro Kimura für seine freundliche Anleitung und steten Ratschläge, die mir bei der Ausführung dieser Arbeit zuteil geworden sind, meinen herzlichsten Dank aussprechen. Ferner möchte ich Herrn T. Hanya für seine eifrige Hilfe und Herrn Kumanosuke Kataoka, von der Thermalquellen-Vereinigung Ito, und Herrn M. Saito für ihre Freundlichkeit, herzlichst danken. Dem Unterrichtsministerium sei gedankt für die Gewährung einer Unterstützung zur Anregung wissenschaftlicher Forschung. Der Kaiserlichen Akademie der Wissenschaft sind wir für ihre finanzielle Unterstützung zu grossem Dank verpflichtet.

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